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Toxins, Defensive Compounds and Drugs from Insects

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Introduction

Arthropods and insects as largest groups of organisms with respect to species numbers or biomass contain an incredible number of biologically active low and high molecular compounds (Pietra 2002, Gronquist and Schroeder 2010). When taken by humans these compounds may have medicinal, intoxicating (venoms, toxins), performance enhancing or many other effects and therefore are called drugs. A large fraction of commercially available drugs represent natural products or represent derivatives of natural products (Dettner 2011), wherefore the search for such compounds is very important (Cragg et al. 2012, Tringali 2012). Very often these chemicals are toxic or may deter other animals and are therefore called allomones (defensive compounds) which are advantageous for the sender and disadvantageous for the receiver. With respect to predator prey interactions there exist various antipredator mechanisms in insects. Primary defenses are active before predators perceive prey (passive defenses such as mimicry, crypsis), secondary defenses only work after the predator has discovered its prey. As shown by Witz (1990) secondary defensive mechanisms are more important as compared with primary defensive mechanisms. Among secondary defense mechanisms chemical

defenses are most important as compared with mechanical defense, defensive stridulation or escape (Eisner 1970, Blum 1981, Eisner 2003, Eisner et al. 2005, Dossey 2010, Unkiewicz-Winiarczyk and Gromysz-Kalkowska 2012). These insect natural products usually are produced by the arthropods themselves (Bradshaw 1985, Morgan 2004), in many cases however such compounds originate from dietary plants or animals or might be even produced by symbiotic microorganisms (Pankewitz and Hilker 2008). In many cases the functional significance of these biologically active molecules within insects is unknown. In addition microorganisms isolated from insects may produce biologically active metabolites in the laboratory whereas these products can be never detected within the host insect. [Table 1](#) compiles all insect orders according to Beutel et al. (2014) and their ways of chemical defense. However in this review the term insects includes also entognathous orders which are placed outside of insects by Beutel et al. (2014). Chemical defenses are obviously seldom in primitive and hemimetabolous insects, in contrast especially large holometabolous orders are characterized by a variety of very different chemical defensive mechanisms (Eisner 1970, 2003, Hilker and Meiners 2002, Eisner et al. 2005).

Primitive forms of chemical defenses within insects are represented by regurgitation ([Fig. 1/2](#)) and defecation ([Fig. 1/3](#), [1/4](#) and [Table 1](#); Eisner 1970, Weiss 2006). In many cases both regurgitates and fecal materials not only represent contents of fore- and hindguts but additionally contain behavior-modifying constituents which enhance deterrent and repellent effects of depleted materials. Defecation and regurgitation mechanisms are especially found in grasshoppers ([Table 1](#)), adult beetles, lepidopteran and hymenopteran larvae.

Many insect orders have toxic hemolymph which is often liberated from the interior of the body through reflex bleeding (= autohemorrhage, [Fig. 1/9](#); Beauregard 1890, Eisner 1970, Evans and Schmidt 1990). Such ways to defend are found from Collembola ([Table 1](#)), Plecoptera, Orthoptera, Thysanoptera and Heteroptera. In holometabolous insects these ways to defend are distributed in Neuroptera, Coleoptera ([Fig. 1/9](#)), Lepidoptera, Diptera and Hymenoptera. With respect to egg stages of insects, toxic and behavior-modifying compounds are usually found within the egg or on the egg surface (Hinton 1981, Hilker and Meiners 2002). A lot of other taxa especially from holometabolous orders exhibit various kinds of exocrine glandular defenses ([Fig. 1/1](#), [1/5](#), [1/6](#), [1/8](#)). These exocrine glands are found within body cavities especially at exposed body parts and are sometimes eversible. When the insect developmental stage molts, these exocrine glands with their epicuticular linings must be replaced in the following developmental stage. Such secretions may also be collected in glandular hairs ([Fig. 1/7](#)), and subcuticular cavities as shown

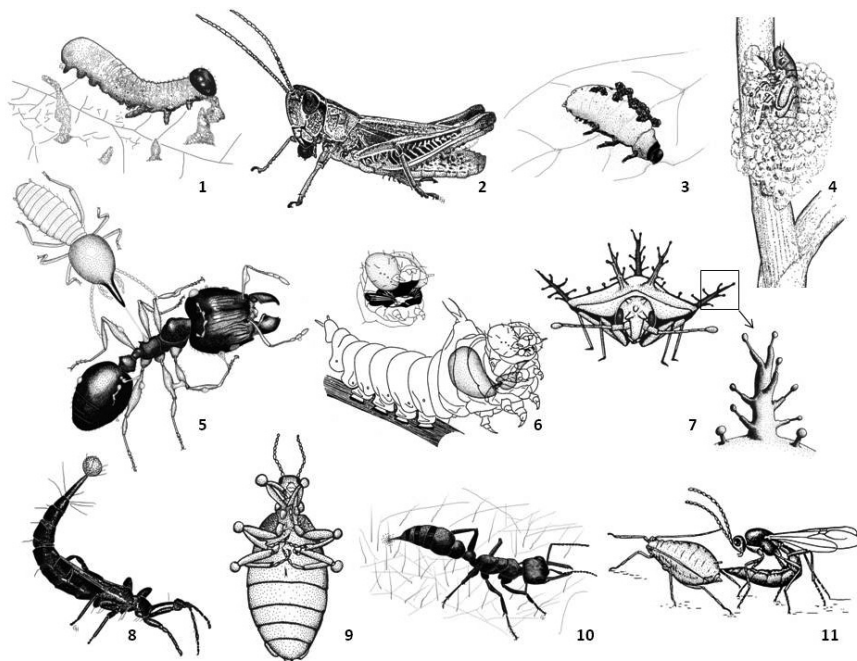


Figure 1. Various mechanisms of chemical defenses in insects (1–11).

1. Herbivorous *Stauronematus* larva (sawflies) depositing foamy pales from their salivary glands around its feeding place. The foam effectively deters ants (taken from a photograph).
2. Regurgitation behavior of a grasshopper (taken from a photograph).
3. Larva of *Leptinotarsa rubiginosa* (Chrysomelidae), the dorsal side of which is covered by feces (beetles; taken from a photograph).
4. Leaf-hopper larva of *Philaenus spumarius* hidden within foamy materials, mainly produced by Malpighian tubules (taken from a photograph).
5. Termite soldier attacking ant species *Pheidole megacephala* (with its sticky secretions from frontal gland). Drawing modified according to Spektrum der Wissenschaft 10 (1983).
6. Ventral prothoracic defensive gland of caterpillar of *Schizura unicornis* (Notodontidae). The inlet figure symbolizes the muscles which may help to aim the defensive spray (according to Whitman et al. 1990).
7. Larva of a tingid bug with its glandular hairs situated at body outgrowths (Scholze and Dettner 1992, unpublished).
8. Thysanopterid species depletes a secretion droplet from exocrine hindgut-glands at its abdominal tip (taken from a photograph).
9. *Meloe violacea* exhibiting thanatosis and reflex-bleeding (liberation of toxic cantharidin containing hemolymph) at femoral-tibian-articulations (according to Meixner 1935).
10. Australian primitive bulldog ant *Myrmecia piliventris* starting to introduce venom with her sting into a human skin (taken from a photograph).
11. Hymenopteran parasitoid *Lysiphlebus testaceipes* introducing her egg into its aphid host. Very often other components are simultaneously injected into the host insect (according to Berland 1951).

Table 1. Survey on insect orders according to Beutel et al. (2014). Apart from worldwide species numbers various strategies of chemical defense are indicated. Marks symbolizing certain defenses only indicate that this kind of defense is present in certain orders irrespective of species numbers.

	Species	chemical defense unknown	poisons bite/sting	hemo-lymph-toxin	reflex bleeding	regurgi-tation	defeca-tion	defensive gland(s)	bacterial/fungal toxins/metabolites	defensive adhesive
Collembola (springtails)	8000			x	x			x		x
Protura (coneheads)	750							x		x
Diplura (dipluran,two-pronged bristletails)	1000	x?								
Archaeognatha (jumping bristletails)	500	x?								
Zygentoma (silverfish)	510	x?								
Ephemeroptera (mayflies)	3000	x								
Odonata (dragonflies, damselflies)	5600	x							x	
Plecoptera (stoneflies)	3500				x					
Dermaptera (earwigs)	2000							x		
Embioptera (webspinners)	360	x?								
Phasmatodea (stick- and leaf insects)	3030							x		
Orthoptera (bush-crickets, crickets, grasshoppers, locusts)	22500			x	x	x	x		x	
Zoraptera (angel insects)	39	x								
Grylloblattodea (ice crawlers, rock crawlers, ice bugs)	32	x								
Mantophasmatodea (heel walkers, gladiators)	18	x								
Mantodea (praying mantises)	2300	x								
Blattodea incl. Isoptera (roaches incl. termites)	7600					x		x		x
Psocoptera (booklice, barkflies and barklice)	5500	x?	x/	x						
Phthiraptera (true lice)	5000	x	x/							
Thysanoptera (thrips, fringe wings)	5822		x/					x		
Auchenorrhyncha (cicadas, leaf-, plant-, frog- and treehoppers)	45000			x	x			x	x	x
Sternorrhyncha (plantlice)	16400									x
Coleorrhyncha (moss bugs)	36	x								
Heteroptera (true bugs)	40000		x/	x	x			x	x	x
Neuroptera (netwinged insects)	6000		x/		x			x	x	
Megaloptera (alderflies, dobsonflies, fishflies)	325					x				
Raphidioptera (snakeflies, camelneck flies)	235	x						x?		
Coleoptera (beetles)	355000		x/	x	x	x	x	x	x	x
Strepsiptera (twisted-winged parasites)	600	x								
Trichoptera (caddisflies)	14500							x		
Lepidoptera (butterflies and moths)	175000			x	x	x	x	x		
Mecoptera (scorpionflies, hanging flies)	550	x?				x				
Siphonaptera (fleas)	2000	x?	x/						x	
Diptera (true flies & midges)	154000		x/	x		x		x		x
Hymenoptera (sawflies, woodwasps, bees, wasps, ants)	132000		x/x	x	x	x	x	x	x	x

in larvae of zygaenid moths (Franzl and Naumann 1985). Finally minute amounts of toxins and venoms may be specifically targeted and applied onto and within targets by stinging or biting (Schmidt 1982, Fitzgerald and Flood 2006). Whereas stinging was only realized in Hymenoptera (Table 1, Fig. 1/10, 1/11; Hermann 1984, Evans and Schmidt 1990), biting structures are more distributed in Phthiraptera, Heteroptera (Table 1), Neuroptera, Coleoptera, Diptera Siphonaptera, and Hymenoptera. Host immune reactions and various allergens were reviewed by Lehane (2005) and Richard and Ledford (2014). Moreover in various insect groups defensive secretions are depleted as adhesives (Fig. 1/5, 1/7), which is compiled in detail by Betz (2010).

Defensive compounds and toxins of arthropods and insects which represent secondary compounds show an extreme chemical and biosynthetic variation (Dettner 2010, Gronquist and Schroeder 2010). In this review fungicidal or bactericidal hemolymph peptides which are produced by the insects themselves are not regarded (see Wiesner and Vilcinskas 2011, Kastin 2013), in contrast microbial products from insect symbionts are discussed. Because of their enormous diversity insects are an interesting source for low molecular compounds but also for larger biomolecules (Blagbrough et al. 1992, Pemberton 1999, Vilcinskas and Gross 2005, Srivastava et al. 2009, Cherniack 2010, Lokeshwari and Shantibala 2010, Dossey 2011) and especially for unusual bacteria and fungi (Dowd 1992). In some cases especially aposematically colored and therefore often toxic insects represent promising candidates for bioprospecting (Helson et al. 2009, Dettner 2011, Vilcinskas 2011).

The following data usually are arranged according to different taxa within an insect order. Within an order sometimes the text was also arranged according to types of exocrine defensive glands.

Natural Compounds According to Insect Orders

There are various insect taxa as Strepsiptera, Raphidioptera, Coleorrhyncha, Phthiraptera, Mantodea, Mantophasmatodea, Grylloblattodea, Zoraptera, Embioptera, Ephemeroptera devoid of toxins, or any way of chemical defense (Table 1). Merely representatives of Phthiraptera (Anoplura) may cause skin lesions (Pediculosis Corporis) and allergic reactions in humans (Alexander 1984). Often these orders comprise only few species or may represent ectoparasites. As expected orders with high species numbers especially holometabolous insects such as Hymenoptera, Lepidoptera are characterized by various ways of chemical defense (see Eisner 1970, Evans and Schmidt 1990). Table 1 illustrates all orders which have few or many ways to defend chemically by gut contents, exocrine

glands, hemolymph toxins, stings, bites or adhesives, in addition insect associated fungal or bacterial metabolites may be of importance.

The following chapters contain those insect orders, where the above mentioned chemical defenses, but also microbial toxins, are present. If there exist reviews concerning behavior modifying chemicals, drugs or toxins of certain insect taxa (e.g., Bettini 1978, Blum 1981, Schulz 2004, 2005, Mebs 2010, Vilcinskis 2011), these compilations are cited for further consultations.

Collembola (springtails)

The jumping ability and detachable hairs or scales represent important modi of defense in this large group of apterygote insects (worldwide 8,000 springtail species). However chemical defense may be of high significance not only in those species which are eyeless or have lost their jumping ability but are at least present in all poduromorph collembolans (Poduridae, Hypogastruridae, Neanuridae, Onychiuridae, Tullbergiidae) and few representatives of entomobryomorphs (e.g., Isotomidae). Some species such as genera *Piroides* or *Corynephora* (Dicyrtomidae) or certain representatives of Neanuridae (e.g., Uchidanurinae) show warning coloration or spine-like colored projections on body surface and some of them may possess club-like defensive glands at abdominal tip. Many species especially of Onychiuridae may release defensive compounds from secretory cells below pseudocells (integumental pores) or via toxic hemolymph by reflex bleeding. On molestation *Tetrodontophora bielanensis* (Onychiuridae) depletes 3 aromatic alkaloids 2,3-dimethoxy-pyrido[2,3-b]pyrazine, 3-isopropyl-2-methoxy-pyrido[2,3-b]pyrazine (Fig. 2), and 2-methoxy-4H-pyrido[2,3-b]pyrazine-3-one (Stransky et al. 1986, Dettner et al. 1996) which act as deterrents against carabid beetles. These compounds are mainly present in pseudocellular secretions but are also recorded in minor amounts from adult hemolymph; larvae only contain traces as was also recorded from *Onychiurus scotarius* and *O. circulans* (Nilsson and Bengtsson 2004). In addition there was identified the open chain tetraterpene lycopane (2,6,10,14,19,23,27,31-octamethyldotriacontane) apart from and in *Tetrodontophora*.

Of the 4 aromatics recorded from *Neanura muscorum* (Neanuridae: phenol, 2-aminophenol, 1,3-dimethoxybenzene, and 2,4-dimethoxyanilin), only 2 aminophenol had a deterrent activity against predatory mite *Pergamasus* (Messer et al. 2000) and was found as a chemotaxonomic marker for Neanurinae subfamily (Porco and Deharveng 2007). 1,3-Dimethoxybenzene was also identified as intraspecific acting alarm pheromone of *Neanura* (Messer et al. 1999), a behavior which was also described from other genera such as *Hypogastrura* (Hypogastruridae),

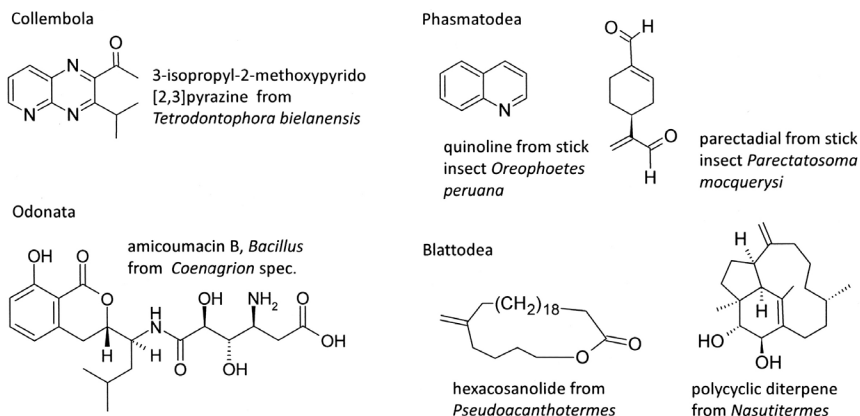


Figure 2. Defensive secretions and hemolymph toxins from Collembola, Phasmatodea and Blattodea. Amicoumacin B represents a microbial product from Odonata.

Folsomia (Isotomidae) and *Megalothorax* (Neelidae) (Purrington et al. 1991). In addition 1,3-dimethoxybenzene and 2,4-dimethoxyaniline have been found as major constituents in hemolymph of *Neanura* adults and in eggs, whereas exuviae of adults only contained small amounts of phenol (Messer et al. 1999). From *Ceratophysella denticulata* (Hypogastruridae; especially from integuments) there were identified 3-hydroxy-4,5-dimethoxy, and 4-hydroxy-3,5-dimethoxy benzoic acids, which represent effective deterrents against *Stenus* predators (Bitzer et al. 2004). Extracts of this species have also been found to act intraspecifically as alarm substances (Pfander and Zettel 2004). From *Podura aquatica* body surfaces finally the new hydrocarbon tetraterpene poduran, with an unusual tricyclo[6.2.0.0]decane system had been identified (Schulz et al. 1997). It seems interesting to denote, that unknown toxic hemolymph constituents of *Folsomia fimetaria* (Isotomuridae) negatively influence reproduction of predatory linyphiid spider *Erigone atra* (Marcussen et al. 1999).

Protura (coneheads)

The minute apterygote and entognathous Protura (750 species) possess huge paired abdominal defensive glands which open on the eighth tergite. When molested the species exude an acid gland material which hardens on contact with air and forms sticky threads (Janetschek 1970, Hansen et al. 2010). The secretion is insoluble in both water and ethanol and contains neutral glycoproteins (Francois and Dallai 1986).

Odonata (dragonflies, damselflies)

Odonata with their worldwide 5,600 species exhibit no chemical defense at all (Table 1). However *Bacillus*-species which were isolated from the gut of *Coenagrion* dragonfly larvae produced the pseudopeptide antibiotic amicoumacin B (Fig. 2) with anti-inflammatory, anti-ulcer and herbicidal activities (Gebhardt et al. 2002, Dettner 2011). It is unknown if gut bacteria of *Coenagrion* produce these compounds *in vivo*.

Plecoptera (stoneflies)

Plecoptera with their worldwide 3,500 species are characterized by terrestrial living adults and aquatic larvae. In two adult (*Pteronarcys proteus*, *Peltoptera maria*; Benfield 1974) and one larval species (*P. dorsata*; Moore and Williams 1990) there was recorded reflex bleeding. When disturbed, adults bleed from intersegmental membranes of coxotrochanteral and tibio-femoral joints. Because there could be recorded neither low molecular compounds nor deterrent-effects of hemolymph it was suggested that the reflex bleeding of stoneflies which is accompanied by an audible popping sound has only a mechanical effect on potential target organisms (Stocks 2008). Zwick (1980) suggests that plecopteran hemolymph primarily acts as an adhesive. In larvae of *P. dorsata* reflex bleeding was observed for the first time in an aquatic insect after contact with benthic tactile crayfish predators (Moore and Williams 1990). In contrast the larva exhibited thanatosis when fish predators appeared.

Dermaptera (earwigs)

Most advanced species of the worldwide known nonparasitic 2,000 Dermaptera species possess abdominal pincers and one or two pairs of defensive gland reservoirs which open on the posterior margins of third and fourth abdominal tergites. The stinking quinoid secretions of earwigs may be discharged as droplets or as a spray which is improved by revolving the abdomen (Eisner 1960, Eisner et al. 2005). The European Earwig *Forficula auricularia* produces methyl- and ethyl-1,4-benzoquinones together with their corresponding hydroquinones (Schildknecht and Weis 1960), whereas the American species *Doru taeniatum* contains methyl- and 2,3-dimethyl-1,4-benzoquinones (as crystals) which are partly dissolved in an organic pentadecane-phase and in a co-occurring aqueous phase. Discharges always occur as quinoid solutions (Eisner et al. 2000). Whether the paired larval glands at the base of the pincers are true defensive glands (Vosseler 1890; defensive glands at the base of larval abdomen are not present) remains to be investigated.

Phasmatodea (stick- and leaf insects)

There have been described more than 3,000 species of Phasmida (stick and leaf insects) whose most important primary defense against predation is crypsis and mimicry. Secondary defenses include startle displays, aposematism, thanatosis, autotomy, sound production or ejection of an irritating spray from a pair of prothoracic exocrine glands (Eisner et al. 2005). Some of the phasmid species are the largest chemically defended insects in the world (Dossey 2010). Especially in males of the genus *Eurycantha* there are found long and hard spines on femora of hind legs and warning odors which originate from the abdominal tips (Seiler et al. 2000). Obviously the defense glands are present in all phasmid suborders. In certain species the secretion may be ejected a well directed beam of secretion which may reach 50 cm in some genera. The secretions represent effective deterrents against arthropods or birds but are also lachrymogenous, cause sneezing and their vapors are painfully irritating when inhaled (Dossey 2010, 2011). Representatives of the genera *Anisomorpha* (Eisner et al. 2005, Dossey 2010), *Autolyca* (Pavan 1975), *Graeffea* (Smith et al. 1979) and *Peruphasma* (McLeod et al. 2007) are characterized by cyclopentanoid monoterpenes as trans-, trans-iridodial, trans-, cis-iridodial, anisomorphal (= dolichodial), peruphasmal or nepetalactone, which are biosynthesized by the phasmids (Meinwald et al. 1966). *Megacrania alpheus* (Chow and Lin 1986, Dossey 2010) produces considerable amounts of actinidine and analogs (probably from iridoids) whereas *Oreophoetes peruana* contains an aqueous emulsion of pure quinoline (Fig. 2) within its defensive glands which represents both repellent and irritant (Eisner et al. 1997). The novel compound parectadial (Fig 2) was recently recorded from *Parectatosoma mocquerysi* from Madagascar, the compound shows cytotoxic and cytostatic properties (Dossey 2010, 2011). In the defensive secretion of *Asceles glaber* there were described the two spiroketals (2S,6R)-(-)(E)-2-methyl-1,7-dioxaspiro[5.5]undecane and 2-ethyl-1,6-dioxaspiro[4.5]decane (Dossey et al. 2012). In contrast *Phyllium westwoodii* sprays its defensive secretion which contains a mixture of 3-isobutyl-2,5-dimethylpyrazine, 2,5-dimethyl-3-(2-methylbutyl)pyrazine and 2,5-dimethyl-3-(3-methylbutyl)pyrazine (Dossey et al. 2009). In *Sipyloidea sipyilus* the defensive secretion contains diethyl ether, acetic acid, benzaldehyde, limonene and benzothiazole (Bouchard et al. 1997), whereas various other species produce methyl-1-hepten-3-one (Dossey 2010). As compared with other chemically defended species the secretion of this Asian species was extraordinary effective (Carlberg 1986).

Orthoptera (bush-crickets, crickets, grasshoppers, locusts)

Among Orthoptera with worldwide about 22,500 species a lot of primary and secondary defensive mechanisms such as crypsis, aposematism, jumping, biting, flight, stridulation or autotomy are realized (see Preston-Mafham 1990, Eisner et al. 2005). Employed chemical defenses are regurgitation (Fig. 1/2), anal discharges or defecation, glandular defensive secretions and internal toxins. Few species may also produce allergens (Richard and Ledford 2014). These various mechanisms were reviewed by Whitman (1990) for most representatives of the suborder Caelifera (grasshoppers). Here especially recent data on chemical defense of *Romalea/Taeniopoda*-grasshoppers, Tridactyloidea (pygmy mole crickets; Caelifera), the sequestration of alkaloids in grasshoppers and chemical defenses of suborder Ensifera are treated.

Both *Romalea* and *Taeniopoda*-species can discharge their defensive secretions from paired metathoracic spiracles respectively from metathoracic tracheal glands (Whitman et al. 1992). Moreover it was shown that adults of *R. guttata* secrete increased amounts of catechol and hydroquinone from their defensive glands when fed especially with *Nepeta*-diet (Snook et al. 1993). In contrast when it was reared on *Allium*-plants, *R. guttata* sequester sulphur volatiles. The defensive secretion in both genera also contained proteinase inhibitors which might act against entomopathogenic fungus (Polanowski et al. 1997). Hatle and Faragher (1998) demonstrated that slow movements may increase survivorship in frog encounters of chemically defended *R. guttata*-specimens. Finally defensive secretion of *T. eques* females may act as sex pheromone eliciting mating behavior in males (Whitman 2008). *R. guttata* was shown to sequester 2,5-dichlorophenol which originates from the herbicide 2,4-D (see Opitz and Müller 2009). In *Anacridium* a sequestration of gallic acid in the integument was reported (Opitz and Müller 2009).

Larvae and both sexes of adult Tridactylidae (more than 200 species; Caelifera) possess paired sternal glands which open laterally on the second abdominal sternum. The chemically unknown defensive secretion may effectively repel *Tetramorium*-ants and *Pardosa*-spiders (Moriya and Ichinose 1988, Moriya 1989). Obviously homologueous defensive glands are present in subterranean sandgropers *Cylindraustralia kochii* (Cylindrachetidae; Houston 2007).

Several grasshopper species are known to excrete or to sequester alkaloids from plants. *Melanoplus* can metabolize toxic pyrrolizidine alkaloids in the gut, yielding more polar metabolites (Ehmke et al. 1989). In addition certain grasshoppers as *Zonocerus elegans* are attracted to pure pyrrolizidine alkaloids such as heliotrine and may even ingest and harbouring them (Boppré et al. 1984). In *Schistocerca emarginata* degrees of

distastefulness through regurgitation depend on the uptake of toxic plant material (Sword 2001).

Exocrine glands and allomones are also found among Ensifera (more than 10,000 species). When disturbed, females of Chinese and European mole-crickets (*Gryllotalpa*; Grylloidea) deplete mucoprotein-containing sticky secretions from their paired anal glands in order to disorientate predators. Since gland extracts are therapeutically used and may improve wound epithelialization and neovascularization in mammals it is of interest to elucidate the chemistry of these gland secretions (Zimmer et al. 2006).

Other partly eversible exocrine defensive glands are typical for representatives of Tettigoniidae (Tettigonioidea; more than 6,000 species) and may be restricted to the thoracic area (Mecopodinae: head/thorax; Pseudophyllinae: procoxae; Rhaphidophoridae: intersegmental membranes), where insectivorous lizards usually seize their prey. A *Vestria*-species belonging to the tropical Katydid emits pyrazines from odoriferous glands near its abdominal tips (Nickle et al. 1996). Other Tettigoniidae may effectively defend themselves by reflex bleeding. Especially in *Eugaster* hemolymph may be squirted up to 80 cm distance (velocity 2–3 m/sec) from bleeding pores at the base of the legs (Grzeschik 1969). In an African king cricket *Onosandrus* spec. it could be shown that defecation is not effective as deterrent against lizards, skinks and toads (Wolf et al. 2006).

Blattodea Inclusive Isoptera (roaches inclusive termites)

There exist various strategies by which cockroaches with their worldwide known more than 4,600 species may escape the attentions of predators. These range from stridulation, flying, quickly running away, coiling into a sphere, diving into water, swimming under water, burrowing, headstanding, to aposematism (warning coloration) and co-occurring aggregations. Sometimes cockroaches may be camouflaged and resemble dead or green leaves, sometimes they may even mimic unpalatable lycid beetles (Preston-Mafham 1990). In addition cockroaches may cause allergic symptoms and bites in humans (Alexander 1984) and often may possess various exocrine glands where allomones are produced. These defensive mechanisms were reviewed 1978 by Roth and Alsop, by Brossut (1983), and partly by Eisner et al. (2005).

Various types of exocrine glands in males and females probably represent defensive glands, the internal surfaces of the gland reservoirs are often covered by setae which may increase evaporation of defensive secretions, when these reservoirs are everted (Beier 1974). In adults and

larvae of some Blattidae the paired **laterocervical glands** produce UV-fluorescent secretions of unknown chemistry (Beier 1974).

Between abdominal spiracles of adults of the primitive Polyphagidae there are situated paired **pleural glands**, which emit complex defensive secretions. In adults of both sexes of *Therea petiveriana* the secretion of these brown eversible pouches serves as allomone and alarm pheromone and contains indole, nonanal, phenol, p-cresol, C₂-, C₄-, C₆-, C₇-, C₉-, C₁₀-C₁₂-carboxylic acids, various fatty acids and the main compounds *N*-3-methylbutylacetamide and *N*-3-methylbutylpropanamide (Farine et al. 2002).

Proteinaceous, slimy secretions which represent mechanically deterrents especially against ants are produced by exocrine **pygidial glands**, which are found on tergites 6, 7 and 10 of adult females and larvae of Blattidae and Blattellidae. There were found no active substances in the slime which suggests that it acts by virtue of its stickyness (Eisner et al. 2005). In larvae of *Megaloblatta blaberoides* the gray sticky proteinaceous secretion on the last abdominal segments and orange spots on its dorsum co-occur with a disturbance stridulation (Schal et al. 1982).

In Blaberidae there are found paired sac-like swellings in the spiracular trunks leading from the lateral trunk to the second spiracles. These swellings which are sometimes also associated with 6th and 7th spiracles represent gland reservoirs of the **tracheal glands** containing various p-quinones, phenols (2-ethylphenol; p-cresol), naphthole, methacrylic and tiglic acids, octanol and 2-decenal (see Brossut 1983), which are directed against arthropods, or pathogenic fungi and bacteria. Force for the ejection of secretion as a fine mist is provided by air from the internal tracheal air sacs (Eisner et al. 2005). Since the lining of the tracheal glands is shed after molting, larvae are defenseless at that time. In contrast freshly molted adult females are attractive for males and during subsequent copulations they may even derive profit from male gland-discharges since males are capable for chemical defense (Wytenbach and Eisner 2001). In freshly molted *Diploptera*-adults Baldwin et al. (1990) showed that refilling of defensive glands with quinones was delayed which might be due to a competition for aromatic amino acids between cuticular and defensive quinone synthesis.

Larvae and adults of Blattidae possess unpaired **ventral** or **sternal glands** (sometimes with various lobules) which open between 6th and 7th sternites. Volatile secretions with 2-methylene butanal, *E*-2-hexenal, various short branched carboxylic acids or 2-acetyl-4-methylbutyrolactone (Brossut 1983) represent effective defensive secretions which may be sprayed and may repel predatory vertebrates and invertebrates. Nonvolatile fractions contain gluconic acid, gluconolactone and glucose of unknown biological activity. The organic fraction of this secretion, which may even be ejected

was analyzed in *Eurycotis floridana* (Farine et al. 1997) and was shown to contain 40 compounds, especially 3-ethoxyhexanal, 3-hydroxyhexanal, ((*E*)-1-pentenyl)-4-propyl-1,3-dioxane, and 3-(*E*)-2-hexenoxyhexanal are unusual for insects. It was shown that the *Eurycotis*-secretion acts against small mammals however single individuals were capable of neutralizing this chemical defense by thrusting the roach's abdomen into the substrate (O'Connell and Reagle 2002). In other species of the genera *Periplaneta* and *Blatta* there were recorded 3-hydroxy-2-butanone (= acetoin), p-cresol, 2- and 4-ethylphenol, 4-vinylphenol, and indol (Takegawa and Takahashi 1990). In *E. floridana* it was additionally shown, that (*E*)-2-hexenal, (*E*)-2-hexenol and (*E*)-2-hexenoic acid are preferentially biosynthesized de novo from labelled acetate (Farine et al. 2000). The secretion proved to be an effective deterrent against mice, ants and other cockroaches (Turnbull and Fashing 2002).

Between 5th and 6th tergites in larvae and adults (both sexes) of Blattinae (Blattidae) there open **paired tergal glands**, the secretions of which represent allomones with 2- and 3-pentanone, 3-octanone, 2,3,4-methylcyclohexanone or α -terpineol. The toxic mixtures can be oozed out or spread from the body side being stimulated. In *Deropeltis wahlbergi* females and larvae assume a rigid stance just before ejection of secretion. In the fully wing males, wings are rotated upwards before secretion is emitted (Eisner et al. 2005). Residual defensive secretions on the abdominal tergites may fortify the repellency of the secretion for a longer time.

Because bioluminescence may also represent an effective chemical defensive system it should be noted that there were discovered luminescent cockroaches in the canopy forests of South America (Vršanský et al. 2012, see Oba, this book).

Female cockroaches deposit their eggs into an ootheca which is produced by female accessory glands. The protein arthropodin is hardened by tanning with ortho-quinones which are formed by oxidation of protocatechuic acid. It might be that calcium oxalate which can form up to 15% of the dry weight of the ootheca represents a chemical defensive agent (Wigglesworth 1974).

Termites with their worldwide 3,000 known species are today integrated within Blattodea. As social insects with high biomass values they have various enemies such as specialized mammals, ants but also so-called guests which may parasitize within the termite colonies. Therefore, representatives of Isoptera developed various defensive mechanisms. Especially their subterranean life and the development of the soldier caste represent effective defensive strategies. However worker termites are not defenseless. Mainly the soldiers, the percentage of which is between 4–9% in primitive termites and increases to 20–30% of individuals in highly

developed families, are mechanically and especially chemically defended. Whereas chemical defensive compounds are found in salivary glands in lower termites, higher termites especially use their frontal glands (Fig. 1/5). The secretion of this unpaired gland may flow over a discharging gutter or groove to the mandibles or the labrum where it contacts the wounds. Very often the opening of the frontal gland is enlarged into a tube and the secretion can be squirted and distributed with a kind of brush. In various species salivary glands and especially frontal glands extend into the abdomen and may release their defensive secretion (together with gut contents) by autothysis (gland rupture) (“Kamikaze-soldiers”) and abdominal dehiscence (intestinal rupture). In addition and especially in workers there was observed both defecation and regurgitation of defensive fluids in termites.

Many exocrine compounds and especially allomones of termites were compiled by Wheeler and Duffield (1988) and Laurent et al. (2005). Various aspects of chemical defense in termites were reported by Prestwich (1983, 1984), Howse (1984) or Quennedey (1984). Apart from some general remarks, here only recent data on termite chemical defense are compiled.

According to their functions termite defensive secretions are regarded as antihealants and irritants (especially mono- and sesquiterpenes, diterpenes, quinones), contact poisons (e.g., nitroalkenes, vinyl ketones, β -ketoaldehydes; Spanton and Prestwich 1982), alarm substances or glues (aqueous lipid-glycoprotein-mucopolysaccharide).

As examples for aggressive termite gland products there is figured hexacosanolide (Fig. 2) from *Pseudoacanthotermes spiniger*. The compound from the salivary gland paralyzes and sometimes may kill aggressors (Laurent et al. 2005). Moreover Fig. 2 shows a polycyclic diterpene (Laurent et al. 2005) from the frontal glands of *Nasutitermes* and *Trinervitermes* soldiers. The secretions are irritating and usually act as glues.

Secretions from glands localized at base of mandibles and from cibarial gland may penetrate the wound inflicted by the mandibles and are considered as auxiliary defense organs. If tarsal glands might contribute to chemical defense has to be investigated. Chemical defensive secretions are produced in the paired salivary (non-volatile, aqueous secretions) and unpaired frontal glands (especially developed in Rhinotermitidae, Termitidae). The frontal gland secretions represent terpenoids (mono-, di- and sesquiterpenes: hydrocarbons and oxygenated products), acetate-derived compounds (quinones, macrocyclic lactones, alkanes, nitroalkenes, vinyl ketones, ketoaldehydes) and other chemicals from amino acid and/or carbohydrate metabolism (proteins, mucopolysaccharides) (Prestwich 1984). Ohta et al. (2007) discovered novel free ceramides as components of the frontal gland of *Coptotermes formosanus*.

Psocoptera (booklice, barkflies and barklice)

Psocids or barklice with about 5,500 species worldwide may produce human allergens, but have no distinct defensive organs (Dathe 2003, Parker 1982). Only certain larvae possess glandular hairs to which particles of algae, lichens or feces may adhere. It seems also possible that psocoptera may sequester aromatic compounds which are typical for lichens. Therefore especially these stages but also all stages of many other species are camouflaged, although few species may be brightly colored. Many species can produce silk from glands which are associated with the labium (see Neuenfeldt and Scheibel, this book). These constructs may protect from predators, desiccation or wetting. Howard and Lord (2003) reported that the booklice *Liposcelis bostrychophila* was unaffected by three entomopathogenic fungi of broad host range. They suggested that certain kinds of the cucicular lipids of these booklice such as C₁₅- and C₁₆-aldehydes, C₁₆- to C₂₂-amides and C₁₆- and C₁₈-fatty acids have fungistatic properties.

Thysanoptera (thrips, fringe wings)

Worldwide there are described more than 5,800 Thysanoptera (thrips)-species. Many of these minute insects with body lengths of 1–3 mm may cause considerable economic damage through sucking and by potential transfer of viruses, bacteria and fungi. Often Thysanoptera take up plant juices (suborder Terebrantia), however many species may also feed on fungal spores (Tubulifera: Phlaeothripidae) or represent true arthropod predators. In addition many thysanopteran species may cause skin lesions in humans due to thrip bites (Alexander 1984).

There exist various defense strategies of thrips-species against natural arthropod predators (e.g., ants, mites), ectoparasitic mites, internal parasites or entomopathogenic fungi. Most specimens escape by jumping and flying, they may feign death or may release a defensive secretion. Anal secretions have been described as sources for various allomones and alarm pheromones (e.g., perillene). When attacked scorpion-like thrips flex the tips of their abdomina, which represent true applicators due to their setae, towards aggressors and exude a droplet of anal fluid (Fig. 1/8; Howard et al. 1983, Tschuch et al. 2004). Obviously long setae cover the droplet, whereas short setae prevent spreading of the secretion (Tschuch et al. 2004). Apart from bactericidal secretions the chemical defense of thrips therefore acts either via odor (repellency) or via topical application (contact activity; deterency). In some cases active compounds may spread over the surface of the aggressor (Moritz 2006). Gall-inhabiting species may use their volatile anal droplets as fumigants (Blum 1991). The anal

defensive secretion may consist of one compound or even can contain up to 11 constituents. Concerning chemical defense in Thysanoptera there exist two compilations (Blum 1991, Moritz 2006).

Various saturated and unsaturated hydrocarbons very often represent major allomones in a considerable number of Thysanoptera species. From dodecane to heptadecane all saturated hydrocarbons are especially found in gall-inhabiting taxa. There were also recorded various alkenes such as (Z)-7-pentadecene, (Z)-8-heptadecene, (Z)-9-octadecene, (Z)-9-nonadecene, or nonadecadiene (Blum 1991, Suzuki et al. 2004, Moritz 2006). Phenole was identified from two genera *Arrhenothrips* and *Euryaplothrips* (Blum 1991, Moritz 2006). There were additionally recorded two aromatic aldehydes from Thysanoptera: 2-hydroxy-6-methyl-benzaldehyde (*Xylaplothrips*) and phenylacetaldehyde (*Arrhenothrips*, *Euryaplothrips*, Blum 1991, Moritz 2006). In 2 *Holothrips*-species there could be even identified 3-butanoyl-4-hydroxy-6-methyl-2H-pyran-2-one (Suzuki et al. 1993). Thrips species and especially representatives of Idalothripinae may also emit three naphthoquinones which are partly known as allelopathic agents: juglone (*Bactrothrips*), 7-methyl- and 2-methyl-juglone (*Ponticulothrips*, *Dolichotherips*; Blum 1991, Moritz 2006).

Among esters various acetates [C10, C12, C14, C16, C18, C20 acetates, dodecadienylacetate, (Z)-9-hexadienyl- and (Z)-11,19-eicosadienylacetate; Moritz 2006], together with hexadecylbutanoate are found in anal secretions of Thysanoptera (Blum 1981, 1991, Tschuch et al. 2008). Several of these esters which are sometimes classified as solvents seem to represent true repellents [e.g., (11Z)-11,19-eicosadienylacetate in *Suocerathrips linguis*; Howard et al. 1987, Teerling et al. 1993, Tschuch et al. 2002a,b, Suzuki et al. 2004]. Under natural temperature conditions solid esters such as stearyl acetate may be dissolved in the fluidal (11Z)-11,19-eicosadienylacetate (Tschuch et al. 2004, 2005). *Bagnalliella yuccae* contained 0.12 µg (larva) to 0.27 µg (adult) of γ -decalactone per specimen which is not present in leaves of the hostplant but probably synthesized in the hindgut (Howard et al. 1983, Haga et al. 1989). 4-Octadec-9-enolide was recorded from secretion of *Euryaplothrips* (Blum 1991). The aromatic lactone mellein was recorded from genus *Haplothrips* (Blum et al. 1992).

Among the various terpenes which were especially recorded from gall-inducing Phlaeothripidae, the furanomonoterpene perillene was found in various genera (*Arrhenothrips*, *Leeuwenia*, *Liothrips*, *Oidanothrips*, *Varshneyia*, *Xylaplothrips*, Blum 1981, Suzuki et al. 1986, 1988, Blum 1991, Moritz 2006). The perillene isomer 3-methyl(3-methyl-2-buten-1-yl)-furan (= rose furane) is present in *Arrhenothrips* and was recorded for the first time in animals. Other terpenes are the unstable dialdehyde β -acaridial, which was found in the genera *Gynaikothrips*, *Liothrips*, and *Varshneyia*, but is also known from mites (Suzuki et al. 1988, 1989). Further terpenes

constitute β -myrcene (*Dolichotherips*, *Thilotherips*), dolichodial (e.g., *Callocothrips*, *Leeuwenia*), α - and β -pinene (*Dolichotherips*), neral, geranial (*Eugynotherips*) and the sesquiterpene caryophyllene (*Dolichotherips*).

Apart from short chained carboxylic acids 2-methylbutanoic acid (*Varshneyia*) and 3-methylbutanoic acid (*Dinotherips*), there were found several long chained saturated (C8, C10, C12) and unsaturated acids [(*E*)-4-decenoic acid, (*Z*)-5- and (*E*)-3-dodecenoic acids, (*Z*)-5-tetradecenoic acid, dodecadienoic acid, and 5,8-tetradecadienoic acid]. The anal droplets of the eusocial gall-inducing species *Kladotherips intermedius* contained unsaturated wax esters, short chain fatty acids and 7-octenoic, 8-nonenic- and 9-decenoic acids (De Facci et al. 2014).

Auchenorrhyncha (cicadas, leaf-, plant-, frog- and treehoppers)

Chemical defense mechanisms of Auchenorrhyncha were only recorded from few taxa as compared with 45,000 species worldwide known. From few species it is reported that they contain the toxic terpenanhydrid cantharidin (see Fig. 4; Hemp and Dettner 2001). This was proved by Feng et al. (1988) and Dettner (1997) for *Lycorma delicatula*. In the case of *Huechys sanguinea* the presence of cantharidin was suggested (Juanjie et al. 1995). It is unknown whether the terpenanhydrid is sequestered from animals or biosynthesized by the cicadas.

Moreover, reflex bleeding was reported from 44 species of Neotropical froghoppers from the tribes Tomaspidini and Ischnorhinini where adults are able to exude hemolymph from pretarsal pads by rupture of membranes (Peck 2000, Stocks 2008). The authors suggested that this behavior is defensive because many species have an aposematic coloration and may emit warning odors such as pyrazines (Guilford et al. 1987). These pyrazine odors significantly make visually conspicuous prey aversive to bird predators (Lindström et al. 2001). The role of the volatile mevalolactone which is emitted by *Psammotettix alienus* is remarkable (Alla et al. 2002). Finally from dried juvenile cicadas, which are used in Chinese medicine, there was registered the peptide cicadine with antifungal activity (Wang and Ng 2002).

An unusual behavior is reported from nymphs of spittlebugs (Mello et al. 1987). The larvae secrete a froth which surrounds their body and within which they are living and at the same time are protected from desiccation and from harmful environmental factors (Fig. 1/4). By Mello et al. (1987) it was shown that the froth contains ten polypeptides (most of them glycopeptides), acid proteoglycans. Del Campo et al. (2011) analyzed *Aphrophora*-froth and identified fatty-acid derived alcohols, γ -lactones, 1-monoacylglycerol, pinitol and poly-3-hydroxybutyrate. The froth repelled ants but showed no topical irritancy against cockroaches.

In contrast Auchenorrhyncha harbored a lot of symbiotic microorganisms with biologically active molecules. *Nilaparvata lugens* contains both *Bacillus*-species producing the decapeptide antibiotic polymyxin M₁ (Fig. 3) and unknown bacteria which produce the polyketide antibiotic andrimid (Fig. 3). Andrimid and similar compounds such as moiramides, which were isolated from various marine organisms and their bacteria represent broad spectrum antibacterials, which inhibit the fatty acid biosynthesis in bacteria (Dettner 2011). In the meantime the gene cluster responsible for andrimid-biosynthesis was identified in *Enterobacter* (Yu et al. 2005). Pyoluteorine (Fig. 3), a pyrrol-antibiotic and polyketide was isolated from *Sogatella*-plant hoppers (Delphacidae). It is also produced by *Pseudomonas*-species (Kenny et al. 1989). Finally from endosymbionts of a White-blackd planthopper species diacetylphloroglucinol (Fig. 3), an antimicrobial, fungicidal and phytotoxic polyketid was isolated (Kenny et al. 1989). Recently a gene cluster for synthesis of this interesting compound was identified in *Pseudomonas fluorescens* (see Dettner 2011).

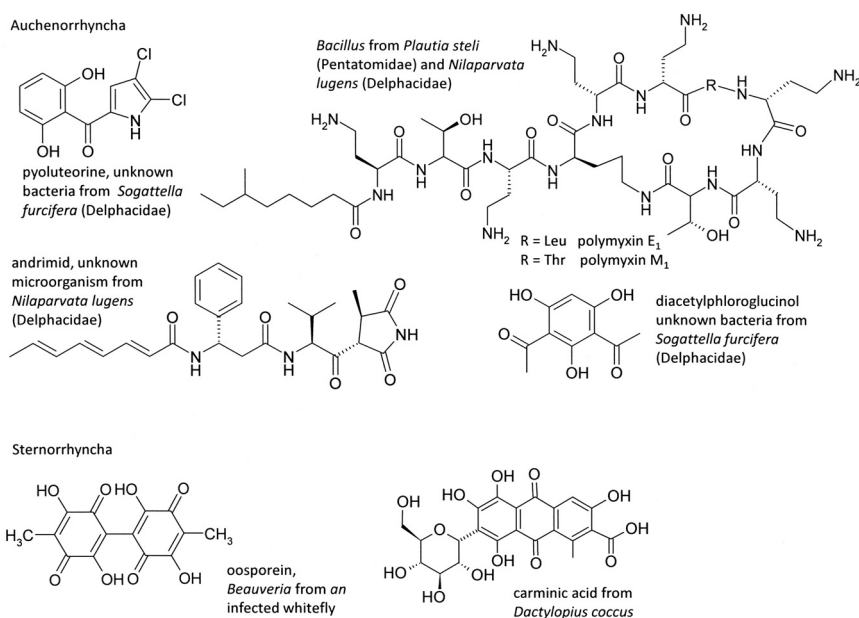


Figure 3. Microbial metabolites from Auchenorrhyncha and Sternorrhyncha. Carminic acid from *Dactylopius coccus* represents a hemolymph toxin.

Sternorrhyncha (plantlice)

From the worldwide known 16,400 species of plantlice various defense strategies are reported (Dixon 1997). Many taxa are known to sequester toxic compounds from plants. Important metabolites are pyrrolizidine alkaloids which may be sequestered by *Ceroplastes* (Coccidae) or *Aphis* (Aphididae) (see Opitz and Müller 2009). Moreover, sequestration of quinolizidine alkaloids was reported from the genera *Macrosiphum* and *Aphis* (Aphididae), whereas *Brevicoryne* and *Lipaphis* (Aphididae) may sequester glucosinolates (Opitz and Müller 2009). Sequestration of both toxicants protected the plantlice from attacks by carabid or ladybird beetles. Several plantlice may also sequester cardiac (*Aphis*) and iridoid glycosides (*Acyrtosiphon*) (Opitz and Müller 2009).

As reported by Eisner (1970, 2003) and Eisner et al. (2005) wax production may be an important defensive mechanism against plantlice predators.

A well-known important defensive mechanism is due to the red dye of various homopteran species. The most important compound is represented by carminic acid (Fig. 3) which may be found together with other compounds in the genera *Kermes*, *Dactylopius*, *Porphyrophora*, *Kerria*, *Lakshadia*, *Acantococcus*, *Ceroplastes*, *Eriococcus* and *Tachardia*. The biological role of these deterrents has been thoroughly reviewed by Eisner (1970, 2003) and Eisner et al. (2005). Larvae from other predaceous insects such as *Hyperaspis* coccinelids, *Leucopis* flies and *Laetilia* pyralid caterpillars ingest carminic acid from their plantlice prey, sequester the compound and emit the deterrent fluid when they are disturbed (Eisner et al. 1994). Chemical data concerning these insect pigments (kermes acid, flavokermes acid, lacain acids A–D, erythrolaccin, desoxyerythrolaccin, isoerythrolaccin, ceroalbinic acid, 7-hydroxyemodin and emodin) are found in Brown (1975) and Schweppe (1993). From *Beauveria* species (Ascomycota) which originated from an infected whitefly there was isolated the red toxic and antifungal dibenzoquinone pigment oosporein (Fig. 3; Eyal et al. 1994, Dettner 2011).

When attacked by predators many aphids release a cornicle secretion. On the one hand these secretions contain alarm pheromones that alert other members of the colony. In addition these cornicle secretion may also threaten an attacker (Moayeri et al. 2014). It was reported by Callow et al. (1973) that cornicle secretion contained triglycerides, especially with hexanoic, sorbic, myristic and palmitic acids. Obviously the waxy material may be kept in a liquid state by a solvent which evaporates rapidly in the air which would explain the rapid change of cornicle wax from the liquid to a crystalline state. Another explanation would be that the liquid wax is in a supercooled state and that foreign material provides a seeding nucleus for the rapid crystallization (Edwards 1966).

Finally it is reported that larvae of genus *Aleurocanthus* possess certain dorsal spines which release through apical orifices sticky, viscous retentive droplets. Carver (1991) suggested that the droplets have a defensive function and also serve for gluing the exuviae of the previous instar to the glandular spines. The semiochemistry of aphids was recently reviewed by Pickett et al. (2013).

Heteroptera (true bugs)

There exist various reviews with respect to exocrinology and especially defensive chemistry of true bugs which comprise 40,000 species worldwide and possess a lot of exocrine structures including secretory hairs (Fig. 1/7). In 1978 (Dazzini Valcurone and Pavan 1978, Weatherston and Percy 1978a) and 1988 (Aldrich 1988) gave a complete survey on glands and chemical defensive systems of Heteroptera. The volatiles (including allomones) and especially pheromones of true bugs were reviewed by Millar (2005). Morphological details and glandular structures such as metathoracic scent glands, abdominal glands, ventral and sternal glands, brindley's glands, accessory glands, pronotal exocrine glands and secretory hairs (Fig. 1/7) were compiled by Staddon (1979) and Aldrich (1988). A survey of the glandular defensive compounds was presented by Aldrich (1988) and Millar (2005). It is interesting to denote that secretions from the brindley gland of Reduviidae have defensive functions (Aldrich 1988, Audino et al. 2007). Moreover there were identified unusual acetogenins which are produced by secretory hairs in larvae and adults of lace bugs (Tingidae) and are directed against bacteria, fungi, nematodes and other predators (see Millar 2005). Apart from Tingidae secretory hairs are also known from larvae of stilt bugs (Berytidae) and assassin bugs (Reduviidae). From the saliva of both selected Reduviidae and Cimicidae there have been isolated several anticoagulant and allergenic proteins (Richard and Ledford 2014). In addition bites of many heteropterans are painful (Alexander 1984, Schaefer and Panizzi 2000).

Heteroptera are also important with respect to sequestration of organic compounds which might be present in both hemolymph and exocrine glands. Several species as *Largus rufipennis* and *Neocoryphus bicrucis* may sequester pyrrolizidine alkaloids (see Opitz and Müller 2009). Moreover, Heteroptera can selectively take up and enrich (Opitz and Müller 2009) tropane alkaloids (*Acanthocoris*), cyanogenic glycosides, cyanolipids (*Leptocoris*, *Jadera*), glucosinolates (*Murgancia*), cardiac glycosides (*Oncopeltus*, *Caenocoris*, *Spilostethus*) and certain toxic phorbol esters (*Pachycoris*). In addition various heteropteran species (Lygaeidae, Miridae, Tingidae; see Hemp and Dettner 2001) pharmacophagously take up the toxic terpene anhydride cantharidin from meloid and oedemerid beetles (Dettner 1997, Hemp and Dettner 2001).

A lot of Heteroptera possess powerful venoms which are directed against both vertebrates (Schmidt 1982) and invertebrates such as insects (Sahayaraj and Vinothkanna 2011). Clinical reactions to bug bites are discussed by Alexander (1984). Further informations are compiled in Schaefer and Panizzi (2000). Several of these enzymes could be characterized chemically (giant water bugs Belostomatidae: Swart et al. 2006; Reduviidae: Sahayaraj and Vinothkanna 2011). Few species are also known to produce allergens (Richard and Ledford 2014).

Several heteropteran species produce unusual defensive compounds. For example representatives of aquatic Belostomatidae contain deoxycorticosterone, pregnenolone, progesterone in their cephalic glands (Lokensgard et al. 1993) and resemble defensive secretions of dytiscid water beetles (Dettner 2014). There are several reports on unusual interactions between heteropteran defensive secretions and other arthropods. For example (*E*)-2-octenal or (*E*)-2-decenal may attract male crab spiders (Thomisidae) or kleptoparasitic flies (Milichiidae, Chloropidae) (Aldrich and Barros 1995). Furthermore a male *Satyrium*-butterfly was attracted to a female *Banasa*-stink bug (Moskowitz 2002). Finally *Trissolcus*-egg parasitoids (Scelionidae) are attracted to α,β -unsaturated aldehydes from heteropteran defensive glands (Mattiacci et al. 1993).

Heteroptera may also contain interesting microorganisms apart from true symbionts from mycetomes. A *Bacillus* species which was isolated from *Plautia stali* (Pentatomidae) produced the cyclic decapeptide antibiotic polymyxin E₁ (Fig. 3, Kenny et al. 1989).

Neuroptera (netwinged insects)

There exist about 6,000 neuropteran species worldwide (probably 10,000). Chemical defense, although actually poorly understood, seems widespread in all developmental stages of this holometabolous, mainly predatory insect order.

Eggs of many neuropteran species (Berothidae, Mantispidae, Chrysopidae) are usually deposited on the top of a slender stalk or egg pedicel which is formed from a gelatinous fluid from female accessory glands. In certain species such as *Ceraeochrysa smithi* the stalks are coated by droplets of an oily secretion produced by females, which contains oleic acid, butanal, decanal, pentadecanal, and isopropyl myristate (Eisner et al. 1996, Eisner et al. 2005). After hatching from the egg, young *Ceraeochrysa*-larvae avoid body contact with these ant repellents by ingesting the fluid (Eisner et al. 1996).

During prey capture neuropteran larvae (e.g., Osmylidae, Chrysopidae, Ascalaphidae, Hemerobiidae, Myrmeleontidae) inject toxic secretions as

regurgitants into prey in order to paralyze and to kill it. In ant lion larvae (genus *Myrmeleon*; Myrmeleontidae) which feed on liquefied internal components of insect prey production of toxins was observed. These are derived from both *Myrmeleon*-larvae and their bacterial symbionts and they contribute to the prey's paralyzation and death. Larval toxins were identified as a larval ALMB-toxin (Yoshida et al. 1999) and as a paralytic 165-167 kDa polypeptide, which was even more active as a paralyzing agent than tetrodotoxin (Matsuda et al. 1995). There were also identified compounds produced by bacterial isolates cultured from larval fore- and midguts of *M. bore*, gut parts which are not connected with the hindgut. *Bacillus*- and *Enterobacter*-species from the insect larvae may produce a paralyzing toxin which is a homolog of GroEL, a protective heat-shock protein known as molecular chaperone (Yoshida et al. 2001). The symbiotic bacteria also synthesize an insecticidal sphingomyelinase C (34 kDa) which probably acts via its phospholipid-degrading activity (Nishiwaki et al. 2004). Finally a *Bacillus sphaericus*-isolate from the crops of *Myrmeleon bore* produced a novel insecticidal pore-forming 53 kDa-toxin, named sphaericolysin (Nishiwaki et al. 2007). The role of two low molecular compounds, two isoindoline alkaloids from *Myrmeleon bore* is unknown (Nakatani et al. 2006). It is known from east Africa that larvae of ant lions (Myrmeleontidae) are preferably collected by young girls, are brought into contact with the girls breasts and depleted secretions together with mechanically stimulations may stimulate the breast growth in adolescent girls (Kutalek and Kassa 2005). Until now it is unknown what kind of constituents in the regurgitant of larvae of ant lions may stimulate breast growth in the young girls (Dettner 2014).

From Australian Chrysopidae-larvae (which are usually camouflaged by cast skins or other materials) there were reported injuries to humans, because the sharp-pointed jaws are capable of piercing human skin (Southcott 1991). Effects for humans are local pain with erythema and a local papule, lasting few hours to a day.

Apart from these toxins, neuropteran larvae may show other means of defense. Chrysopid larvae very often cover themselves with remnants of their insect prey, trichomes of certain plants, lichens or even waxy filaments (Eisner et al. 2005). For locomotion or anchoring, chrysopid larvae of various genera (e.g., *Ceraeochrysa* = *Chrysopa*, *Chrysoperla*, *Eremochrysa*) often use anal droplets of a sticky proteinaceous secretion. In addition after molestations the larvae move their flexible abdomen in any direction and expose a fluid droplet of a defensive secretion to the aggressor (LaMunyon and Adams 1987). The secretion which is probably produced in the Malpighian tubules contains precursors of prepupal silk and is stored in the hindgut. It is extremely repulsive to ants and shows a paralyzation within 15 minutes. It cannot spread and quickly dries at the

surface of ants especially the antennae. There the material can be quickly removed by cleansing behavior, because it is highly soluble in the saliva of ants (LaMunyon and Adams 1987). It is interesting to denote that larvae of the genus *Lomamyia* (Berthidae) which live subterraneously and feed on certain termites may release an aerosol from their abdominal tips which paralyzes their termite prey (Johnson and Hagen 1981). Finally larvae of *Mantispa uhleri* (Mantispidae; closely related with Berthidae) which live in spider cocoons and feed on spider eggs use unknown chemicals (aggressive allomones) in order to halt the development of spider eggs (Redborg 1983).

Adults of Neuroptera exhibit various mechanisms of chemical defense. Even the characteristic waxy secretions of adult Coniopterygidae seem to represent a true chemical and mechanical defense. Within genus *Semidalis* it was shown that apart from the eyes the total body was covered with waxy particles consisting of tetracosanoic acid (Nelson et al. 2003). However neuropteran adults often possess exocrine glands located in the pro- and metathorax and in the abdomina, which often are functionally and chemically unknown (Güsten 1996).

The paired prothoracic glands of Chrysopidae open at the frontal margin of the sometimes redly colored prothorax and obviously represent defensive glands (Güsten and Dettner 1992). In many species investigated 1-tridecene (Blum et al. 1973) and (Z)-4-tridecene (Güsten and Dettner 1992) represent the main constituents. Depending on species other compounds of the often noxious and skunklike odor are octanoic acid, skatole (= 3-methyl indole), terpenoids, hydrocarbons and amides (Güsten and Dettner 1992). There were observed no sexual dimorphisms, neither in gland morphology nor in secretion chemistry in 20 species (Güsten 1996). The most primitive species investigated of genus *Nineta* only synthesized the alkene which could indicate a spreading of regurgitants or feces together with the alkene (Güsten and Dettner 1992). As a whole, dendrograms revealing phylogeny of Chrysopidae based on both electrophoretic data and glandular chemistry were very similar (Güsten and Dettner 1992). Repellent effects of a chrysopid secretion were registered not only against mammals but also against ants (Blum et al. 1973). In the meantime it was shown that (Z)-4-tridecene elicited a significant EAD-response (single sensillum recordings) in *Chrysoperla carnea* and an avoidance behavior in predatory ants (Zhu et al. 2000). It was shown that also inodorous species (without skatole) possess the paired prothoracic glands (Güsten and Dettner 1992).

Also in Osmylidae paired eversible prothoracic gland vesicles have been described in both sexes which supports the homology of the structure in both families (Güsten 1996). On molestation of adults of *Osmylus spec.* a disagreeable odor of unknown chemistry is perceivable.

In the meantime there were detected further semiochemicals from *Chrysopa*-species together with EAD-responses. Antennae of both sexes of *Chrysopa oculata* responded to following three compounds from male abdomina: nonanal, nonanoic acid, and (1*R*, 2*S*, 5*R*, 8*R*)-iridodial. Both sexes of this species were especially attracted by (1*R*, 2*S*, 5*R*, 8*R*)-iridodial (Zhang et al. 2004, Chauhan et al. 2007). Even (1*R*, 4*aS*, 7*S*, 7*aR*)-nepetalactol (an aphid sex pheromone component) showed a weak attraction especially to males. Thoracic extracts of both sexes contained the antennal-stimulatory 1-tridecene and the EAD-inactive skatole (Zhang et al. 2004). Male specific epidermal glands in *C. oculata* have been described as potential pheromone glands (Zhang et al. 2004). This corresponds with the data of Güsten (1996) that abdominal glands in seven neuropteran families (including Chrysopidae) confined to males could represent pheromone glands.

In adults of Myrmeleontidae the paired metathoracic gland system was morphologically analyzed in 10 species from 6 tribes (Güsten 1998). It was also described that the setae-bearing knob (pilula axillaries) projecting from the base of male hindwings and fitting into the reservoir opening of the metathoracic gland serves for evaporation of the secretion (Güsten 1996). Besides species with smaller female glands, there are also species with female glands absent, species with glands lacking in both sexes and species with glands equally developed in both sexes. Therefore, it was suggested that the metathoracic glands in Myrmeleontidae were originally defensive glands and later developed separately in both sexes, that means from defensive secretions to species-specific attractants and aphrodisiacs (Güsten 1998).

Megaloptera (alderflies, dobsonflies, fishflies)

Among Megaloptera with their worldwide known 325 species larvae and prepupae of *Neohermes* can vomit a noxious-smelling liquid when disturbed (Smith 1970) and therefore exhibit a very pronounced avoidance reaction on encountering others. Adults, such as females of genus *Corydalus* also can bite (Parfin 1952).

Coleoptera (beetles)

Defensive substances and pheromones of beetles with their worldwide known 355,000 species as largest order of life on Earth have been reviewed recently (Dettner 1987, Francke and Dettner 2005, Laurent et al. 2005). All kind of chemical defenses (Table 1) are realized in Coleoptera, including defecation (Fig. 1/3) and reflex bleeding (hemolymph toxins, Fig. 1/9). In addition several species produce skin eruptions in mammals, which may

be due to pederin from the genus *Paederus* (Staphylinidae), cantharidin from Meloidae and Oedemeridae or serrated hairs of larvae from Dermestidae (Alexander 1984). Other results from Coleoptera are mainly from Eisner (1970, 2003), Eisner et al. (2005), Weatherston and Percy (1978b), Blum (1981) or from Hilker and Meiners (2002).

Concerning their pygidial gland chemistry two representatives of the aedeophagous family Trachypachidae (*Trachypachus gibbsii*, *T. slevini*) seem closer to Geadephaga (aliphatic constituents: isopropyl methacrylate and ethacrylate, 2- and 3-hexanone, isovaleric-, isobutyric-, 2-methylbutyric-, methacrylic-, ethacrylic- and nonanoic acids, (Z)-7- and (Z)-9-tricosene, (Z)-7- and (Z)-9-pentacosene, pentacosadiene) than to Hydradephaga (aromatics: 2-phenethylethanol, 2-phenethyl methacrylate- and ethacrylate) (Attygalle et al. 2004). Further data on pygidial glands of Carabidae were presented by Will et al. (2000). In *Chlaenius cordicollis* (Carabidae) the variability of the pygidial gland secretion was assessed zoogeographically with 3-methylphenol as main constituent, together with 2,5-dimethylphenol, 3-ethylphenol, 2,3-dimethylphenol and 3,4-dimethylphenol (Holliday et al. 2012). In addition representatives of Carabidae and Paussidae can eject blistering gland contents from their pygidial glands which may produce skin irritations (Alexander 1984).

Adult whirligig beetles (Gyrinidae) and predaceous diving beetles (Dytiscidae) respectively their defensive secretions with norsesquiterpens (gyrinids) and hormone-like steroids (Dytiscids) are used in order to stimulate breast growth in young girls in East Africa (Kutalek and Kassa 2005). For further discussions see Dettner (1985, 2014). One unusual steroid mirasorvone from the aposematically colored water beetle *Thermonectus marmoratus* is figured in Fig. 5. New data on the volatiles (3-methyl-1-butanal, 2-methyl-1-propanol, 3-methyl-1-butanol, 6-methyl-5-hepten-2-on) of pygidial glands of Gyrinidae were compiled by Ivarsson et al. (1996). The pygidial gland chemistry of Haliplidae with 3-hydroxyoctanoic and decanoic acids, phenylacetic acid, 4-hydroxyphenylacetic acid or phenyllactic acid was reviewed by Dettner and Böhner (2009). A complete compilation of pygidial and prothoracic defensive glands constituents of Dytiscidae with many steroids and other terpenes is presented by Dettner (2014).

The Staphylinidae or rove beetles produce a diverse array of defensive chemicals which was illustrated by Dettner (1987, 1993) and Francke and Dettner (2005). A detailed analysis of anal and oral secretions and head space of *Nicrophorus vespilloides* (carrion beetle) revealed 34 compounds which partly showed antimicrobial activities (Degenkolb et al. 2011). Within representatives of rove beetle subfamily Steninae there were found various new chemical structures from the paired anal defensive glands. Apart from stenusin and norstenusin there were identified three

new pyridine alkaloids [especially 3-(2-methyl-1-propenyl)pyridine] and the unusual cicindelone (Lusebrink et al. 2009, Müller et al. 2012). It is remarkable that the spreading potential and skimming behavior of selected *Steninae* varies considerably (Lang et al. 2012). In addition there were found intrageneric differences in the four stereoisomers of stenusin (the spreading alkaloid) in *Stenus*-species (Lusebrink et al. 2007). The ratio of the four stereoisomers (2'R,3R)-, (2'S,3R)-, (2'S,3S)-, and (2'R,3S)-stenusine varied depending on species respectively subgenera. The multifunctional role, ecological significance and evolution of the pygidial gland system in *Steninae* was reviewed by Schierling et al. (2013) and Schierling and Dettner (2013).

Concerning rove beetle genus *Paederus* (Paederinae) the transfer of endosymbionts of genus *Pseudomonas* from females to eggs was reported by Kador et al. (2011). The bacteria which are located in the female accessory glands and produce the cytotoxic polyketide pederin are smeared on the egg surface and must be taken by the hatching larvae. Pederin with the biosynthetically related pederone and pseudopederin are shown in Fig. 4. Many aspects on biological activities and medicinal chemistry of polyketids of pederin/mycalamide family are discussed by Mosey and Floreancig (2012).

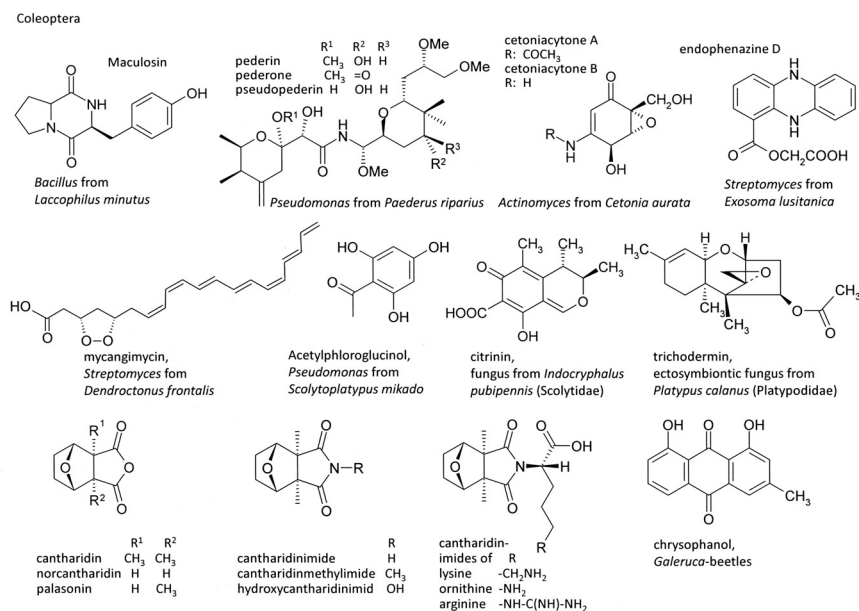


Figure 4. Bacterial and fungal (citrinin, trichodermin) metabolites from Coleoptera. Coleopteran hemolymph toxins are illustrated in the third row.

The semiochemistry of various beetle groups was recently studied in detail. These groups with defensive glands and allomones are Scarabaeoidea (Vuts et al. 2014), Erotylidae (Drilling and Dettner 2010, Drilling et al. 2013) and Coccinellidae (King and Meinwald 1996, Laurent et al. 2005). In Scarabaeidae there were reported repellents such as β -necrodol or butyl sorbate (Vuts et al. 2014). Moreover pygidial gland secretions of neotropical *Canthon*-dung rollers contain compounds such as geraniol, guaiacol or phenol which act as deterrents against predatory *Camponotus*-ants (Cortez et al. 2012). Remarkably *Canthon*-carrion beetles are attracted to defensive volatile secretions of diplopod species such as HCN, benzaldehyde or various benzoquinones (Bedoussac et al. 2007, Dettner 2010). Beetles of the genera *Calopteron* and *Lycus* (Lycidae) are well known to be chemically protected which seems mainly due to the novel octadeca-5E,7E-dien-9-ynoic acid (= lycidic acid). As warning odor they produce 2-methoxy-3-isopropylpyrazine (Eisner et al. 2008). Remarkably certain cerambycid beetle taxa such as *Elytroleptus* mimic these lycid beetles and feed on them (Eisner et al. 2008). Several defensive compounds and natural products of Coccinellidae have characteristic structures. This is illustrated in Fig. 5, where nitrogen containing molecules as epilachnene from *Epilachna varivestis*, psylloborine A from *Psyllobora 22-punctata*, chilocorine B from *Chilocorus cacti*, euphococcinine, a pyrrolidinoxazolidinine and two piperidines from *Epilachna* are seen. From *Harmonia axyridis* there have been reported various inhalant allergens (Richard and Ledford 2014). In addition this neozoic beetle is protected by alkaloids such as

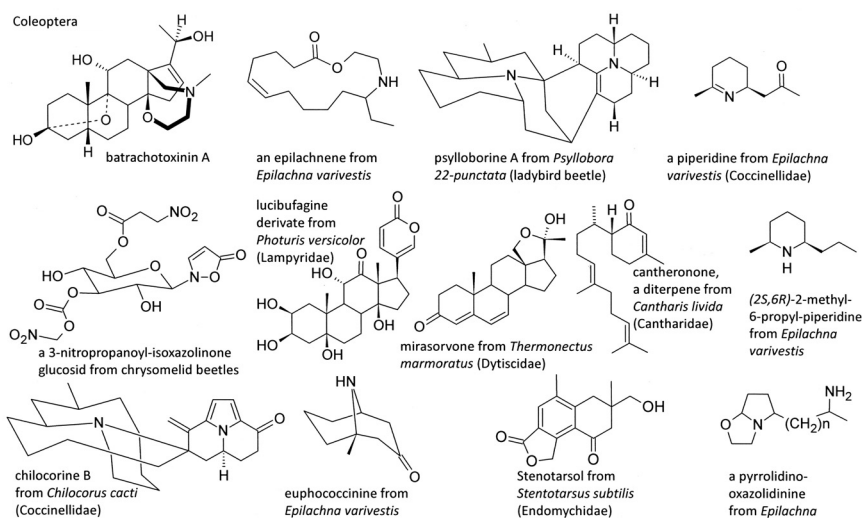


Figure 5. Hemolymph toxins and glandular defensive compounds (mirasorvone, 3-nitropropanoyl-isoxazolinone glucosid) from Coleoptera.

harmonine and (S)-3-hydroxypiperidin-2-one and contains various 2-alkyl-3-methoxypyrazines (Sloggett et al. 2011). Remarkably the harmonine-alkaloid titer per beetle is correlated with the percentage area of orange body color. From a phylogenetically primitive subfamily both the larval and pupal defensive compounds from secretory hairs have been described by Deyrup et al. (2014). Representatives of the genus *Delphastus* produce both isoprenoids such as (*E,E*)-2,6-diacetoxygermacr-1(10),4-diene and various polyketides such as catalpyrones H-J. Both types of compounds which differ from typical N-containing defensive compounds are biosynthesized endogenously (Deyrup et al. 2014). In *Hippodamia convergens* 2-isobutyl-3-methoxypyrazine which was interpreted as warning odor efficiently acted as aggregation pheromone (Wheeler and Cardé 2013). In *Stenotarsus subtilis*, a representative of handsome fungus beetles (Endomychidae, about 1,300 species) the sister group of Coccinellidae, there could be identified stenotarsol (Fig. 5; Laurent et al. 2005) with a new type of terpene skeleton. Obviously endomychid beetles are characterized by a unique chemical defense which is different from that of Coccinellidae (Laurent et al. 2005).

Larvae of certain fireflies (Lampyridae) are unique in that they are subaquatic and possess fork-shaped glands laterally from meso- and metathorax which can be everted on molestation. Simultaneously there was observed thanatosis, a glowing from paired abdominal glands and a pine oil-like odor which is partly due to the presence of terpinolene and γ -terpinene (Fu et al. 2007, Oba et al. 2011, Oba, this book). By capillary NMR-spectroscopy in few specimens of the lampyrid beetle *Lucidota atra* there could be identified 12 new steroidal pyrones (see also lucibufagine from *Photuris*, Fig. 5) and one compound which instead of a pyrone substituent contains a pentenoic acid amide moiety. As compared with known firefly steroidal pyrones these steroids show a great variation in oxidation of the steroid skeleton and mostly possess a *trans*-fused A-B ring system (Gronquist et al. 2005). Recently the presence of steroidal pyrones could also be confirmed for Eurasian species *Lampyris noctiluca* (Tyler et al. 2008).

Beetles of *Choresine pulchra* (Malachiidae) were shown to contain various batrachotoxins such as batrachotoxin, homobatrachotoxin, batrachotoxin A (and its *cis*-O- and *trans*-O-crotonates, and acetate; Fig. 5) which are probably transferred to passerine birds (*Pitohui*-birds) and render them toxic (Dumbacher et al. 2004). It is unknown whether the beetles biosynthesize their own batrachotoxins or get them from prey or symbiotic microorganisms.

From Australian jewel beetles (Buprestidae) there were isolated bitter tasting acylglycosides buprestin A and B (Brown et al. 1985) with a deterrent activity against ants (Moore and Brown 1985). There was subsequently developed a chemical and enzymatic approach to these

buprestins A and B (Schramm et al. 2006). In addition there were identified various buprestins with altered O-6 acyl moieties in *Anthaxia hungarica* and *Chalcophora mariana* by incorporation of hydroxylated cinnamoyl residues (buprestin D, E, F) or substituted benzoyl moieties (buprestin G, G; Ryczek et al. 2009).

In the meantime there was analyzed the transcriptome of odoriferous defensive stink glands of *Tribolium castaneum* (Tenebrionidae; Li et al. 2013). In this pioneering study 29 genes (38%) presented strong visible phenotypes, while 67% genes showed alterations of at least one gland content. Three of this genes which showed quinone-less phenotypes were isolated, molecularly characterized, their expressions identified in both types of the secretory gland cells and their function determined. The authors also showed that quinoic secretions are necessary to inhibit bacterial or fungal growth in the beetle cultivars. Phylogenetic analyses of this genes indicate that they have evolved independently and specifically for chemical defense in beetles.

The chemical defensive systems of chrysomelid beetles and their developmental stages are fascinating. Several important metabolites are compiled in Pasteels et al. (2004) and Laurent et al. (2005) and Fig. 5 (3-nitropropanoyl-isoxazolinone glucoside), however a thorough view is presented in a separate bookchapter by Burse and Boland (this book).

Recently it was shown that the defensive structures in larvae of Sermlyni (Galerucinae) resemble exocrine defensive glands in Chrysomelinae (the putative sister group of Galerucinae) evolved independently (Bünnige and Hilker 2005, Bünnige et al. 2008). In *Agelastica alni*-larvae the sac-like cuticular invaginations near the abdominal spiracles obviously represent defensive structures (Bünnige and Hilker 1999).

When disturbed, larvae of cassidine chrysomelid beetles can aim and wave shields against attackers, which are made of cast skin and feces. In *Chelymorpha alternans* it was shown for the first time, that the chlorophyll catabolite phaeophorbide a exhibits a deterrent activity against ants. Shields of one beetle larva contained more than 100 µg of the porphyrinic compound (Vencl et al. 2009). The chemical ecology of longhorned beetles (Cerambycidae) was reviewed by Weatherston and Percy (1978b), Allison et al. (2004) and Francke and Dettner (2005). In addition there were identified various repellents and deterrents (Allison et al. 2004) such as (-)-germacrene D, conophthorin, hexanal, Z-3-hexenol, ethylbenzene, guaiacol, nonylaldehyde, p-dimethoxybenzene, myrcene, (E)-β-ocimene, α-cubebene, (E)-4,8-dimethylnona-1,3,7-triene, (E)-2-hexen-1-ol and (E)-2-hexenal.

Sequestration of plant secondary compounds by herbivorous beetles according to Opitz and Müller (2009) seems variable and there is a range from phenolic glycosides (larvae of *Chrysomela*, *Phratora*),

prenylated aromatic compounds, cycasin (curculionid beetle *Rhopalotria*), pyrrolizidine alkaloids (chrysomelid beetles: *Platyphora*, *Longitarsus*, *Oreina*; *Chauliognathus* Cantharidae), cardiac glycosides (*Chrysochus*), cucurbitacines (*Diabrotica*, *Acalymma*), iridoidglycosides (*Dibolia*), to isoprenoids (*Platyphora* spec.). Keefover-Ring (2013) studied the fecal shields of larvae of tortoise species *Physonota* which feed on *Monarda* plants (Lamiaceae). It was evident that those plants subjected to herbivory emitted higher titers of volatiles, which are incorporated into the larval fecal shields of *Physonota* larvae. Attraction of the following species to the toxic animal derived cantharidin (including subsequent sequestration) was reported from Anthicidae (many species from genera *Acanthinus*, *Anthicus*, *Aulacoderus*, *Cordicomus*, *Cyclodinus*, *Endomia*, *Formicilla*, *Formicomus*, *Hirticomus*, *Mecynotarsus*, *Microhoria*, *Notoxus*, *Omonadus*, *Pseudoleptaleus*, *Pseudonotoxus*, *Sapintus*, *Tenuicomus*, *Vacusus*, *Trichananca*, *Tomoderus*), Endomychidae (*Aphorista*, *Danae*, *Lycoperdina*, *Xenomycetes*), Cleridae (*Cymatodera*, *Pallenothriocera*), Chrysomelidae (*Aristobrotica*, *Barombiella*), Pyrochroidae (many species from genera *Anisotria*, *Pedilus*, *Neopyrochroa*, *Pyrochroa*, *Schizotus*), and Staphylinidae (*Eusphalerum*) (Dettner et al. 1997, Hemp and Dettner 2001).

The polyketides chrysazin, chrysophanol (Fig. 4), dithranol and chrysarobin are found especially in eggs but also in other developmental stages of leaf beetles of Galerucinae. By treatment of the female beetles of *Galeruca tanacetii* with antimicrobial substances it could be shown that freshly laid eggs contained these polyketides, indicating that these compounds are produced by beetle enzymes and not by endosymbiotic microorganisms (Pankewitz et al. 2007a). The bioactive anthraquinone chrysophanol represents the first product of a polyketid synthase that is built up by more than one polyketid folding mode (Bringmann et al. 2006). In actinomycetes the cyclization follows mode S (from *Streptomyces*) in contrast in higher plants, fungi and insects it is formed via folding mode F (referring to fungi). In addition there was observed no increase of polyketid titer in freshly laid eggs as compared with freshly hatched larvae. Instead a significant decrease in total amounts of dithranol and chrysophanol from egg deposition in autumn to spring 5 months later was registered (Pankewitz and Hilker 2006). As already mentioned leaf beetles of the taxon Galerucini transfer antimicrobially active 1,8-dihydroxylated anthraquinones and anthrones into their eggs. It was shown that obligatory, cytoplasmatically inherited α -Proteobacteria, respectively certain genotypes of these bacteria may settle such eggs in spite of the presence of antimicrobics (Pankewitz et al. 2007b). Generally a polyketid synthases (PKS) in insects may have evolved from insect fatty acid synthases (FAS; Pankewitz and Hilker 2008).

Coleoptera host a lot of bacteria and fungi, which may produce interesting natural compounds in the laboratory. However the role of these constituents in their host remains unknown. The phytotoxic and cytotoxic diketopiperazine maculosin (Fig. 4) was isolated from *Bacillus pumilus* and from *Laccophilus minutus*-foregut (Gebhardt et al. 2002). Pederin, pederone, pseudopederin from *Pseudomonas* (Fig. 4) from *Paederus* represent important tumor-inhibiting compounds (see above). Their role in beetles as spider-deterrents was unequivocally proved (Kellner and Dettner 1996). Cetoniacytone A and B (Fig. 4) were released from an *Actinomyces*-species which was isolated from hind guts of *Cetonia aurata* (Schlörke et al. 2002). Both compounds show significant growth inhibition against hepatocellular carcinoma and breast adenocarcinoma. Further research in these *Cetonia*-strains resulted in isolation of a gene cluster responsible for biosynthesis of cetoniacytone A (Wu et al. 2009).

Endophenazines such as endophenazine D (Fig. 4) were produced from *Streptomyces annulatus* which were isolated from *Exosoma*-chrysolimid crops (Gebhardt et al. 2002). These compounds inhibited growth of *Botrytis* and showed herbicidal properties. Cantheronone (Fig. 5) represents an interesting diterpene enone which was isolated from total body extracts of *Cantharis livida* (see Gronquist and Schroeder 2010). Mycangimycin (Bode 2011) (Fig. 4), a polyene peroxide with strong antifungal activity was produced from a *Streptomyces* strain isolated from *Dendroctonus frontalis*. The polyketid metabolite acetylphloroglucinol (Fig. 4) was isolated from *Pseudomonas* from *Sciolytoplatus mikado*. Citrinine (Fig. 4), an antibiotic pentaketide was isolated from an unknown fungus from *Indocryphalus pubipennis* (Scolytidae) (Kenny et al. 1989). Finally trichodermin (Fig. 4) an important inhibitor of protein synthesis is produced by an ectosymbiotic fungus from *Platypus calanus* (Platypodidae) (Kenny et al. 1989).

Meloid and oedemerid beetles possess unusual terpenoid compounds apart from cantharidin (Fig. 4). In addition these Coleoptera may contain palasonin, cantharidinimide, cantharidinmethyylimide, hydroxycantharidinimide, and cantharidinimides of lysine, ornithine, and arginine (Fig. 4). All these compounds are very interesting due to their antitumor activities, however, high toxicities due to inhibition of protein phosphatase PP2A prevents their medicinal utilization (Dettner 2011).

Trichoptera (caddisflies)

Chemical defensive systems seem to be present in various taxa of the worldwide known 14,500 species of caddisflies. Many larval caddisflies exhibit case-building from silk glands as a primary defense behavior. In addition when disturbed the aquatic larvae of the genera *Apatania* and *Apataniana* (Limnephilidae) release a defensive fluid from an eversible

prothoracic gland which shows a paralyzing effect against small invertebrate predators (e.g., other trichopteran larvae such as *Rhyacophila* sp.) but seems ineffective against larger targets such as plecopteran larvae or fishes (Wagner et al. 1990). The secretion contains C₇ to C₁₄-carboxylic acids with the major constituents 5-octenoic-, octanoic-, decanoic-, 3-dodecenoic-, 3,5-dodecadienoic- and 3,5,7,11-tetradecatetrenoic acids (Wagner et al. 1990).

When adult caddisflies are handled they can cause allergic responses (asthma, dermatitis; Bowles 1992). In addition depending on species they may often emit a distinct odor which can be ascribed as sweet or foul skatolic. A pair of sac-like glands from the 5th abdominal sternum but also glands from the 4th segment represent the source of many volatiles such as p-cresol, indole, skatole (*Pycnopsyche*, Limnephilidae; Duffield et al. 1977), 6-methyl-nonan-3-one (Hesperophylax, Limnephilidae; Bjostadt et al. 1996), 2-heptan-2-one, heptan-2-ol, nonan-2-one, nonan-2-ol (*Rhyacophila*, Rhyacophilidae; Duffield 1981, Löfstedt et al. 1994), hexanoic- and octanoic acids, heptan-2-ol, acetophenone (*Rhyacophila*, Rhyacophilidae; Ansteeg and Dettner 1991, Löfstedt et al. 1994), 2-methylbutanoic acid (*Polycentropus*, Polycentropodidae; Ansteeg and Dettner 1991), 1-pentanol, 1-octanol, 3-methyl-2-heptanone, 2-phenylethanol (*Phryganea*, Phryganeidae; Ansteeg and Dettner 1991), heptane-2-one, (S)-heptan-2-ol, nonan-2-one, nonan-2-one (*Hydropsyche*, Hydropsychidae; Löfstedt et al. 1994), (S)-nonan-2-ol (*Molanna*, Molannidae; Löfstedt et al. 2008), (S)-4-methyl-3-heptanone, (4S,6S)-4,6-dimethyl-3-octanone, (4S,6S)-4,6-dimethyl-3-nonanone (*Potamophylax*, *Glyphotaelius*, Limnephilidae; Bergmann et al. 2001), (1R,3S,5S,7S)-1-ethyl-3,5,7-trimethyl-2,8-dioxabicyclo[3.2.1] octane and 1,3-diethyl-4,6-dimethyl-2,7-dioxabicyclo[2.2.1] heptane (*Potamophylax*, *Glyphotaelius*, Limnephilidae; Bergmann et al. 2004).

As evidenced by field trapping experiments, in many cases these volatiles such as methylcarbinols and methylketones have pheromonal function and show antennal response in males (Löfstedt et al. 2008). However in other species chemically deviating compounds may represent defensive secretions which are emitted in larger amounts (Ivanov and Melnitsky 1999). Löfstedt et al. (2008) argued that pheromone components such as methylcarbinols and methylketones, which are produced in sternum glands of segment 5 may be a basal character in both Trichoptera and Lepidoptera which constitute the superorder Amphiesmenoptera. For example the short chain alcohols and corresponding methyl ketones identified from caddisflies are similar to the sex pheromone components identified from the archaic moth families Eriocraniidae and Nepticulidae. Several observations indicate that not all abdominal gland secretions in Trichoptera may represent pheromones: The 5th segment glands of certain caddisflies are developed in both sexes (although containing different

compounds in males and females; Ansteeg and Dettner 1991). Moreover homologous abdominal glands may be present in both sexes of primitive lepidopteran Micropterigidae, but no pheromone communication at all was shown especially in this group (Kozlov and Zvereva 1999).

Lepidoptera (butterflies and moths)

Butterflies and moths with their 175,000 species worldwide are characterized by various systems to defend themselves chemically. Important reviews covering chemical defenses of all lepidopteran developmental stages are from Pavan and Valcurone Dazzini (1976), Brower (1984), Rothschild (1985) or Hallberg and Poppy (2003). As herbivorous insects they are at first important in sequestration of toxic plant chemicals (Trigo 2000, Nishida 2002, Opitz and Müller 2009). The authors report on natural compounds such as various acids, phenolic glycosides, cycasin, pyrrolizidin alkaloids, quinolizidine alkaloids, tropane alkaloids, amarillidaceae alkaloids, cyanogenic glycosides but also cardiac glycosides, iridoid glycosides or isoprenoids such as *Podocarpus* lactones. Chemical defense mechanisms of lepidopteran species were in detail reviewed by Delgado Quiroz (1978) and Dekker (1984). Valuable informations were also given by Eisner et al. (2005) and Laurent et al. (2005). Just as tenthredinid larvae (Hymenoptera) plant feeding lepidopteran larvae show many mechanisms of chemical defense as was reviewed by Bowers (1993), Hallberg and Poppy (2003), Vegliante and Hasenfuss (2012), Dyer and Smilanich (2012) and Greeney et al. (2012). As an example there are shown ventral prothoracic defensive glands of *Schizura unicornis* caterpillars (Fig. 1/6) which usually produce formic acid mixed with various lipophiles (Weatherston et al. 1986). Within larvae there were found osmeteria, thoracic and abdominal defensive glands or oral secretions. In osmeteria of *Papilio glaucus* larvae the ecological, ontogenetic and genetic variations in gland chemistry was investigated by Frankfater et al. (2009). There was found a change from terpenoic constituents (directed against ants) to the production of 2-methylbutyric and isobutyric acids (directed against larger predators). Other larvae are characterized by gelatinous coatings which probably acts as deterrents to attack (Epstein et al. 1994) or possess cuticular storage chambers for cyanoglucoside-containing defensive secretions (Franzl and Naumann 1985). In several other families caterpillars are characterized by glandular tracheal nodes (Hings and Byers 1975) or even show sac-like glands (Thyrididae) secreting various deterrents ranging from mandelonitrile to benzaldehyde, benzoic acid, farnesene and 3-methylbutyl-3-methylbutanoate (Darling et al. 2001). Cossidae-larvae of genera *Cossus*, *Zeuzera* and *Xyleutes* possess large mandibular glands which contain strongly smelling defensive compounds such as dienols,

trienols, acetades or 3-hydroxy acids (Pavan and Valcurone Dazzini 1976, Blum 1981). In the genus *Chilecomadia* Reyes-Garcia et al. (2011) identified (Z)-5,13-tetradecadienyl acetate, (Z)-5-tetradecenyl acetate and dodecyl acetate. However the first mentioned acetate seems to represent an aggregation pheromone. Within adult Lepidoptera Hallberg and Poppy (2003) report on tarsal and cervical defensive glands together with ventral hair pencils. In adults of nymphalid butterfly *Agraulis vanillae* there were identified abdominal defensive glands which produce 6-methyl-5-hepten-2-one, 6-methyl-5-hepten-2-ol esters, 1,15-hexadecanediol diacetate and 1,16-hexadecanediol diacetate (Ross et al. 2001). Important aspects of lepidopteran chemical defense are related to urticating hairs or spines of larvae or adults of Zygaenoidea, Bombycoidea, Notodontoidea or Noctuoidea. Various aspects including morphology, chemistry and medicinal aspects were reported by Weidner (1936), Alexander (1984), Deml and Dettner (1993, 1996, 1997, 2003, 2004), Aldrich et al. (1997), Deml (2001, 2003) and Battisti et al. (2011). Larvae of *Pieris rapae* caterpillars possess glandular hairs which bear oily droplets containing unsaturated lipids (mayolenes) which are derived from 11-hydroxylinolenic acid and act as deterrents against ants (Smedley et al. 2002). In some species every year there are numerous accidents in Southamerica because venoms of the *Lonomia* caterpillar cause disseminated and intravascular coagulation and a consumptive coagulopathy which can lead to a hemorrhagic syndrome (Arocha-Piñango et al. 1988, Carrijo-Carvalho and Chudzinski-Tavassi 2007).

Mecoptera (scorpionflies, hanging flies)

When molested representatives of Mecoptera (Scorpion Flies) with about 600 species fall to the ground if they are not camouflaged or show thanatosis (e.g., *Boreus hyemalis*). With their enlarged genital bulb especially males can also defend themselves through biting. Many species emit malodorous digestive fluid from the mouth when they are handled (Kaltenbach 1978).

Siphonaptera (fleas)

The worldwide known 2,000 species are almost all parasitic insects and seem to possess no chemical defensive systems. Salivary allergens of cat fleas have been reported as 18 kDa-proteins (Richard and Ledford 2014). Generally fleas can produce skin lesions in humans (flea bites, papular urticaria, tungiasis; see Alexander 1984). Only in the unique endoparasitic larva of *Uropsylla tasmanica* which parasitizes Tiger cats and Tasmanian devils subdermally, there were identified mandibular glands. Their

function remains unclear, however it was speculated that the secretion may contain anaesthetics to reduce irritations of the hosts (Williams 1986). Finally, from *Bacillus* species which was isolated from the tissue of adults of *Ceratophyllus* spec. the cyclic peptide and bactericidal bacitracin A (Fig. 6) was isolated (Gebhardt et al. 2002).

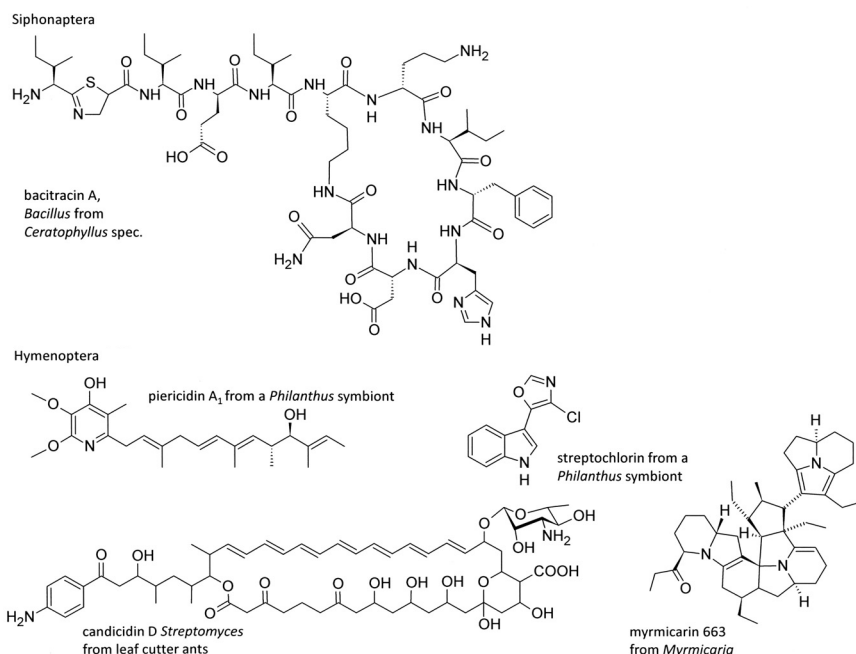


Figure 6. Microbial metabolite from a *Ceratophyllus* flea-species and compounds from Hymenoptera (piericidin A₁ and streptochlorin from a *Philanthus* symbiont; candidicin D from a *Streptomyces* symbiont from leaf cutter ants and gland compound myrmicarin 663 from *Myrmecaria*).

Diptera (true flies and midges)

Although there exist a lot of dipteran species worldwide (about 154,000 species), chemical defenses as far as secondary defenses are concerned, seem to be very rare in this large insect order. Further examples of secondary defense include catalepsy, or rolling and dropping from the plant. In contrast primary defenses such as crypsis, translucence, or bird dropping resemblance may be found in various dipteran taxa (e.g., Rotheray 1986). Certainly careful bionomical investigations may reveal further allomones, toxic or venomous secretions especially in larvae of this large insect order.

Biologically active compounds were registered from pupae of the sandfly *Lutzomyia longipalpis* (Psychodidae). Both squashed pupae and hexane extracts of pupae were deterrent to *Lasius*-ants and their larvae (Dougherty and Hamilton 1996), however, chemical structures are not available. From salivary glands of larvae of predatory gall midges (Cecidomyiidae) such as *Aphidoletes aphidimyza* there could be isolated toxic phenoloxidases which enable them to paralyze their prey aphids (Mayr 1975).

In addition, apneustic larvae of *Forcipomyia* (Ceratopogonidae) possess secretory setae on the dorsal body. These setae produce a hygroscopic secretion which contains 12 free fatty acids (especially oleic, palmitic, palmitoleic and linoleic acid), glycerol and pyroglutamic acid which show antibacterial activities (Urbanek et al. 2012).

Under attack also certain syrphid larvae have been observed in emitting sticky saliva (Rotheray 1986). In addition adults of robber flies (Asilidae) possess a venomous salivary secretion which may kill (secretion from 1-2 specimens) a white mouse or alternatively a locust *Locusta migratoria* (1/2 to 1/126 of a gland; Kahan 1964). There are known various other hematophagous flies the females of which usually require a blood meal to develop eggs and which may produce skin lesions in humans (Alexander 1984). A survey of allergens, anticoagulants and digestive enzymes in mosquitoes (Culicidae), blackflies (Simuliidae), biting midges (Ceratopogonidae), deer- and horseflies (Hippoboscidae, Tabanidae), sandflies (Psychodidae), stable flies (Muscidae), Tsetseflies (Glossinidae) and *Stomoxys calcitrans* is given by Richard and Ledford (2014). Allergic diseases caused by non-biting midges (Chironomidae) are discussed by Cranston (1995).

Adults of many Sepsidae (swing flies) possess stink glands in both sexes which are associated with the rectum. It has been described that the aromatic smelling secretions may deter potential swing fly predators (Bristowe 1979). On the other hand, certain Sepsidae show aggregations, which might be evoked by such glandular secretions. Many volatiles are known to be produced in tephritid flies (Fletcher and Kitching 1995) and are usually reported to act as aggregation or sexual pheromones. In rectal ampullae of males of two gall-forming *Urophora*-species there has been identified 4-methyl-3Z,5-hexadienoic acid (Frenzel et al. 1990), a compound which seems to be also involved in the territorial defense between males.

Autogenous chemicals obviously are found in larvae of certain fungus-gnats (Mycetophilidae), which distribute considerable amounts of oxalic acid along the silken threads of their webs. The silk proteins contain large amounts of alanine, glycine, asparagic and glutaminic acid (Plachter 1979; see Neuenfeldt and Scheibel, this book). Droplets of this strong acid

originate from larval salivary glands and are deposited on both trapping webs of larvae and pupal cocoons (Plachter 1979). Buston (1933) registered pH 1.8 when he tested the web fluid of *Platyura*- and *Ceroplatus*-species and found it toxic against oligochaet species. Pupal secretion of *Rhynchosciara* was also investigated by Terra and de Bianchi (1974). Oxalic acid may protect both larvae and pupae from aggressors (predators, fungi, bacteria) but also can be used by the larvae in order to trap small prey organisms. The origin of the larval oxalic acid remains unclear. However, it seems possible that the adults may take up free oxalic acid which was excreted by wood-rotting basidiomycetes (Munir et al. 2001).

In Diptera there are known several cases of sequestration of defensive chemicals from animal origin. Adults of certain species of Anthomyiidae, Platystomatidae, and especially Ceratopogonidae are attracted to the toxic terpen anhydride cantharidin or naturally occurring cantharidin sources (e.g., dead meloid or oedemerid beetles; canthariphilous insects) and may ingest, detoxify and subsequently sequester this important protein phosphatase inhibitor (Frenzel and Dettner 1994, Dettner 1997).

In tephritid flies (Tephritidae) sequestration of phenylpropanoids such as methyl eugenol but also production of various behavior modifying compounds was reported by Fletcher and Kitching (1995) and Opitz and Müller (2009). Larvae of chamaemyiid flies (Chamaemyiidae) of genus *Leucopis* sequester carminic acid (Fig. 3: 1.12) from cochineal insects which constitute their prey. The larvae eject the compound with their rectal fluid in order to deter ants (Eisner et al. 1994).

It is important to note that bioluminescence for attracting prey and for defense was described in Mycetophilidae as *Arachnocampa*, *Orfelia* (= *Platyura*) or *Keroplatus* (Viviani et al. 2002, Oba this book). It is interesting, that the two bioluminescent systems in *Arachnocampa* and *Orfelia* are different. In *Orfelia* there was found a 140 kDa luciferase, and a luciferin-luciferase reaction, which is activated by dithiothreitol and ascorbic acid, whereas *Arachnocampa* hosts a 36 kDa luciferase, and is characterized by a system activated by adenosine triphosphate (ATP) (Viviani et al. 2002).

Apart from antimicrobial peptides which are found in the hemolymph of various dipteran larvae (e.g., rat-tailed maggot of *Eristalis tenax*; Vilcinskas 2011), blowfly larvae of *Lucilia seriata* may produce various biologically active constituents which are externalized by defecation or vomiting (Vilcinskas 2011, Joop and Vilcinskas this book). Larvae of various dipterans may produce cutaneous or furuncular myiasis by invasion of human skin (Alexander 1984). Moreover many dipteran species from extreme habitats probably harbour a considerable fraction of gut bacteria with interesting activities and microbial products (Kadavy et al. 2000).

Hymenoptera (sawflies, woodwasps, bees, wasps, ants)

With respect to the large insect order of Hymenoptera with worldwide 132,000 species there exist several reviews which cover defensive mechanisms in general (Bischoff 1927) and especially defensive compounds and toxins. A detailed paper on hymenopteran semiochemicals was given by Keeling et al. (2004). Various venoms of hymenopteran and non-hymenopteran species were reviewed by Schmidt (1982). Recent data also focus on defensive odours and venoms of endoparasitoid wasps (Quicke 1997, Asgari and Rivers 2011) and their role in host-parasite interactions (see Fig. 1/11, e.g., Völkl et al. 1994). There have been identified various low molecular volatile compounds from parasitic wasps such as skatole (Gomez et al. 2005), 6-methylhept-5-en-2-one, 3-hydroxy-3-methylbutan-2-one or alkyl spiroacetals (Davies and Madden 1985). Both gland morphological and chemical details of venoms of Apidae, Sphecidae, Pompilidae, Mutillidae, Bethyridae, Vespidae, Braconidae and Formicidae (see Fig. 1/10) are found in Bettini (1978) and Piek (1986), medicinal and pharmacological aspects were presented by Piek 1986 (Vespidae, Apidae, Formicidae), Levick et al. 2000 and Fitzgerald and Flood (2006). In addition allergenic reactions of humans to hymenopteran stings were discussed by Müller (1988), King and Spangfort (2000) or Klotz et al. (2009). Especially honeybee venoms were studied in detail (e.g., Dotimas and Hider 1987). With respect to allomones of Formicidae and other Hymenoptera recent chemical data are presented by Laurent et al. (2005). Formicidae and their venoms were especially reviewed by Numata and Ibuka (1987), Leclercq et al. (2000) and Hoffman (2010). The chemical ecology of bumblebees was summarized by Ayasse and Jarau (2014). As an example Fig. 6 shows the unique structure of one complex alkaloid myrmicarin 663 which has been isolated together with other air- and temperature-sensitive-alkaloids from the poison gland of a *Myrmicaria* species. Compilations covering exocrine compounds of Hymenoptera (e.g., pheromones, allomones) were given by Wheeler and Duffield (1988).

There exist a lot of data with respect to the herbivorous sawfly larvae (Tenthredinidae) which often feed exophytically on leaves. Consequently they are subject to heavy predation and must possess defensive mechanisms such as aposematic coloration, defensive glands, toxic hemolymph, diverticular sacs associated with the foregut or sequestration of toxins against natural enemies. Very often chemical defensive mechanisms in these larvae are accompanied by a group display and many larvae simultaneously rear their hind body. Herbivorous *Stauronematus* larvae even deposit foamy pales from their salivary glands around their feeding place (Fig. 1/1). The foam, which contains proteins, cholesterol and various fatty acids (Zhao et al. 2009) may effectively deters ants or larvae of armyworm *Pseudaletia separata*. Chemical data

with respect to tenthrinid allomones were given by Laurent et al. (2005). Various aspects of biology and defensive behavior of tenthrinid larvae were presented by Schedl (1991), Codella and Raffa (1993), Boevé et al. (2000), Boevé (2006), Petre et al. (2007) and Boevé and Heilporn (2009). It is remarkable that some sawfly larvae are able to deplete small amounts of hemolymph during defense without damaging their integument (Boevé 2009). In addition certain sawfly larvae contain toxic peptides which may cause death of cattle and sheep. For example there could be detected a toxic octapeptide lophyrotomin from sawfly larvae *Lophyrotoma interrupta* (Daly et al. 1993).

Sometimes sequestrations of secondary compounds from plants are also reported from Hymenoptera. The tenthrinid specialist *Rhadinoceraea nodicornis* sequesters ceveratrum alkaloids from *Veratrum album* and may even convert them (see Opitz and Müller 2009). Moreover *Tenthredo grandis* sawfly larvae take up catalpol (iridoid glycoside) from their food. Other species such as *Athalia* spec. sequester neo-clerodane diterpenoids such as clerodendrin D, ajugachin A or athaliadiol from their food plants (see Opitz and Müller 2009) or sequester Furostanol saponins (*Monophadnus*, Prieto et al. 2007). Further tenthrinid species feeding on toxic plants may show reflex bleeding. In addition, hymenopteran parasites maybe attracted to toxic cantharidin (Fig. 4) from meloid and oedemerid beetles (Hemp and Dettner 2001). It is probable that these chemicals which are also present in canthariphilic insects serve as kairomones for these hymenopteran parasitoids. Therefore it seems probable that cantharidin is also sequestered by Braconidae (*Blacus*, *Periltius*, *Streplocera*, *Syrhizus*, *Microtonus*, and *Melittobia*) and Diapriidae (gen. spec.; Hemp and Dettner 2001).

Many Hymenoptera are associated with symbiotic bacteria which produce interesting metabolites. One important example is represented by beewolf digger wasps (*Philanthus*) which cultivate specific symbiotic bacteria (*Streptomyces*) that are incorporated into the cocoon as protection against pathogens (Kroiss et al. 2010). It was reported that the bacteria produce a cocktail of nine antibiotics such as piericidin A₁, an inhibitor of NADH dehydrogenase (Fig. 6) or streptochlorin, which is active against several cancer cell lines (Fig. 6). Another chemically and biologically interesting macrolide is represented by candicidin (Fig. 6), which is used medicinally in the treatment of vulvovaginal candidiasis. *Acromyrmex*—leaf cutting ants are living in an obligate symbiosis with *Leucoagaricus*—fungi which they grow with harvested plant material. These symbiotic fungi serve as major food source of the ants. However certain pathogenic fungi such as *Escovopsis* can overcome the symbiotic fungus and therefore may destroy the whole colony. Now it was discovered (Haeder et al. 2009) that the ants protect *Streptomyces*-species which produce antibiotics such as candicidin D in order to control these parasites. The role of defensive

microbiological symbionts in Hymenoptera was reviewed by Kaltenpoth and Engl (2014).

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References

- Aldrich, J.R. 1988. Chemical ecology of the heteroptera. *Annu. Rev. Entomol.* 33: 211–238.
- Aldrich, J.R. and T.M. Barros. 1995. Chemical attraction of male crab spiders (Araneae, Thomisidae) and kleptoparasitic flies (Diptera, Milichiidae and Chloropidae). *J. Arachnol.* 23: 212–214.
- Aldrich, J.R., P.W. Schaefer, J.E. Oliver, P. Puapoomchareon, C.-J. Lee and R.K. Vander Meer. 1997. Biochemistry of the exocrine secretion from gypsy moth caterpillars (Lepidoptera: Lymantriidae). *Ann. Entomol. Soc. Am.* 90: 75–82.
- Alexander, J.O.D. 1984. *Arthropods and Human Skin*. Springer, Berlin.
- Alla, S., C. Malosse, S. Cassel, P. Rollin and B. Frérot. 2002. La mévalonolactone: un composé volatil produit par *Psammotettix alienus* (Dhb). *Compt. Rend. Biol.* 325: 941–946.
- Allison, J.D., J.H. Borden and S.J. Seybold. 2004. A review of the chemical ecology of the Cerambycidae (Coleoptera). *Chemoecol.* 14: 123–150.
- Ansteeg, O. and K. Dettner. 1991. Chemistry and possible biological significance of secretions from a gland discharging at the 5th abdominal sternit of adult caddisflies (Trichoptera). *Entomol. Gener.* 15: 303–312.
- Arocha-Pinango, C.L., N. Blumenfeld de Bosch, A.L. Nouel, A. Torres, J. Perales, M.E. Alonso, S. de Rodriguez, Z. Carvajal, A. Ojeda, M.L. Tasayco and W. Chitty. 1988. Fibrinolytic and procoagulant agents from a Saturnidae moth caterpillar. pp. 223–240. *In: H.A.U. Pirkle (ed.). Hemostasis and Animal Venoms*. CRC Press, New York.
- Asgari, S. and D.B. Rivers. 2011. Venom proteins from endoparasitic wasps and their role in host-parasite interactions. *Annu. Rev. Entomol.* 56: 313–335.
- Attygalle, A.B., X. Wu, J. Ruzicka, S. Rao, S. Garcia, K. Herath, J. Meinwald, D.R. Maddison and K.W. Will. 2004. Defensive chemical of two species of *Trachypachus* Motschulski. *J. Chem. Ecol.* 30: 577–588.
- Audino, P.G., R.A. Alzogaray, C. Vassena, M. Mashuh, A. Fontán, P. Gatti, A. Martinez, F. Camps, A. Cork and E. Zerba. 2007. Volatile compounds secreted by Brindley's glands of adult *Triatoma infestans*: identification and biological activity of previously unidentified compounds. *J. Vector Ecology* 32: 75–82.
- Ayasse, M. and S. Jarau. 2014. Chemical ecology of bumble bees. *Annu. Rev. Entomol.* 59: 299–319.
- Baldwin, I.T., D.B. Dusenbery and T. Eisner. 1990. Squirtling and refilling: Dynamics of p-benzoquinone production in defensive gland of *Diploptera punctata*. *J. Chem. Ecol.* 16: 2823–2834.
- Battisti, A., G. Holm, B. Fagrell and S. Larsson. 2011. Urticating hairs in arthropods: Their nature and medical significance. *Annu. Rev. Entomol.* 56: 203–220.
- Beauregard, H. 1890. *Les Insectes Vésicants*. F. Alcan, Paris.
- Bedoussac, L., M.E. Favila and R.M. Lopez. 2007. Defensive volatile secretions of two diplopod species attract the carrion ball roller scarab *Canthon morsei* (Coleoptera: Scarabaeidae). *Chemoecol.* 17: 163–167.

- Beier, M. 1974. Blattariae (Schaben). pp 1–127. In: Handbuch der Zoologie, 2. Aufl., Band 4, 2. Hälfte, 2. Teil, Lieferung 13, de Gruyter, Berlin.
- Benfield, E.F. 1974. Authemorrhage in tow stoneflies (Plecoptera) and its effectiveness as a defense mechanism. *Ann. Entomol. Soc. Am.* 67: 739–742.
- Bergmann, J., C. Löfstedt, V.D. Ivanov and W. Francke. 2001. Identification and assignment of the absolute configuration of biologically active methyl-branched ketones from limnephilid caddis flies. *Eur. J. Org. Chem.* 2001: 3175–3179.
- Bergmann, J., C. Löfstedt, V.D. Ivanov and W. Francke. 2004. Identification and synthesis of new bicyclic acetals from caddisflies (Trichoptera). *Tetrahedron Lett.* 45: 3669–3672.
- Berland, L. 1951. Superfamille des Ichneumonoidea. pp. 902–931. In: P.P. Grassé (ed.). *Traité de Zoologie* 10, Fasc. 2. Masson, Paris.
- Bettini, S. 1978. Arthropod Venoms, Handbook of Experimental Pharmacology. Vol. 48. Springer, Berlin.
- Betz, O. 2010. Adhesive exocrine glands in insects: Morphology, ultrastructure, and adhesive secretion. pp. 111–152. In: J. von Byern and I. Grunwald (eds.). *Biological Adhesive Systems*. Springer, Wien.
- Beutel, R.G., F. Friedrich, S.Q. Ge and X.K. Yang. 2014. *Insect Morphology and Phylogeny*. De Gruyter, Berlin.
- Bischoff, H. 1927. *Biologie der Hymenopteren—Eine Naturgeschichte der Hautflügler*. Biologische Studienbücher, Springer, Berlin.
- Bitzer, C., G. Brasse, K. Dettner and S. Schulz. 2004. Benzoic acid derivatives in a hypogastrurid collembolan: temperature-dependent formation and biological significance as deterrents. *J. Chem. Ecol.* 30: 1591–1602.
- Bjostadt, L.B., D.K. Jewett and D.L. Brigham. 1996. Sex pheromone of caddisfly *Hesperophylax occidentalis* (Banks) (Trichoptera: Limnephilidae). *J. Chem. Ecol.* 22: 103–121.
- Blagbrough, I.S., P.T.H. Brackley, M. Bruce, B.W. Bycroft, A.J. Mather, S. Millington, H.L. Sudan and P.N.R. Usherwood. 1992. Arthropod toxins as leads for novel insecticides: an assessment of polyamine amides as glutamate antagonists. *Toxicol.* 30: 303–322.
- Blum, M.S. 1981. *Chemical Defenses of Arthropods*. Academic Press, New York.
- Blum, M.S. 1991. Chemical ecology of the Thysanoptera. pp. 95–112. In: B.L. Parker, L. Bruce, M. Skinner and T. Lewis (eds.). *Towards Understanding Thysanoptera* (Gen. Tech. Rep. NE-147). U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station.
- Blum, M.S., J.B. Wallace and H.M. Fales. 1973. Skatole and tridecene: Identification and possible role in a chrysopid secretion. *Insect Biochem.* 3: 353–357.
- Blum, M.S., R. Footitt and H.M. Fales. 1992. Defensive chemistry and function of the anal exudate of the thrips *Haplothrips leucanthemi*. *Comp. Biochem. Physiol.* 102C: 209–211.
- Bode, H.P. 2011. Insect-associated microorganisms as a source for novel secondary metabolites with therapeutic potential. pp. 77–93. In: A. Vilcinskas (ed.). *Insect Biotechnology, Series: Biologically-Inspired Systems*, Vol. 2. Springer, Dordrecht.
- Boevé, J.-L. 2006. Differing patterns of chemically-mediated defence strategies in Nematinae versus Phymatocerini larvae (Hymenoptera: Tenthredinidae). pp. 63–71. In: S.M. Blank, S. Schmidt and A. Taeger (eds.). *Recent Sawfly Research: Synthesis and Prospects*. Goecke and Evers, Keltern.
- Boevé, J.-L. 2009. Easily damaged integument of some sawflies (Hymenoptera) is part of a defence strategy against predators. pp. 31–43. In: S.N. Gorb (ed.). *Functional Surfaces in Biology*, Vol. 1, Springer, Berlin.
- Boevé, J.-L. and S. Heilporn. 2009. Secretion of the ventral glands in *Craesus* sawfly larvae. *Biochem. System. Ecol.* 36: 836–841.
- Boevé, J.-L., S. Heilporn, K. Dettner and W. Francke. 2000. The secretion of the ventral glands in *Cladius*, *Priophorus* and *Trichiocampus* sawfly larvae. *Biochem. System. Ecol.* 28: 857–864.
- Boppré, M., U. Seibt and W. Wickler. 1984. Pharmacophagy in grasshoppers. *Entomol. Exp. Appl.* 35: 115–117.

- Bouchard, P., C.C. Hsiung and V.A. Yaylayan. 1997. Chemical analysis of defense secretions of *Sipylodea sipylus* and their potential use as repellents against rats. *J. Chem. Ecol.* 23: 2049–2057.
- Bowers, M.D. 1993. Aposematic caterpillars: Life-styles of the warningly colored and unpalatable. pp. 331–371. *In*: N.E. Stamp and T.M. Casey (eds.). *Caterpillars: Ecological and Evolutionary Constraints on Foraging*. Chapman, New York.
- Bowles, D.E. 1992. The medical importance of caddisflies. *Braueria* 19: 24.
- Bradshaw, J.W.S. 1985. Insect Natural Products - Compounds derived from Acetate, Shikimate and Amino Acids. pp. 655–703. *In*: G.A. Kerkut and L.I. Gilbert (eds.). *Comprehensive Insect Physiology, Biochemistry and Pharmacology*, Vol. 11, Pergamon Press, Oxford.
- Bringmann, G., T.F. Noll, T.A.M. Gulder, M. Grüne, M. Dreyer, C. Wilde, F. Pankewitz, M. Hilker, G.D. Payne, A.L. Jones, M. Goodfellow and H.-P. Fiedler. 2006. Different polyketide folding modes converge to an identical molecular architecture. *Nature Chem. Biol.* 2: 429–433.
- Bristowe, W.S. 1979. The mysterious swarms of sepsid flies and their unpalatability to spiders. *Proc. Trans. Brit. Entomol. Nat. Hist. Soc.* 12: 16–19.
- Brossut, R. 1993. Allomonal secretions in cockroaches. *J. Chem. Ecol.* 9: 143–158.
- Brower, L.P. 1984. Chemical defense in butterflies. pp. 109–134. *In*: R.I. Vane-Wright and P.R. Ackery (eds.). *The Biology of Butterflies*. Academic Press, London.
- Brown, K.S. 1975. The chemistry of aphids and scale insects. *Chem. Soc. Rev.* 4: 263–288.
- Brown, W.V., A.J. Jones, M.J. Lacey and B.P. Moore. 1985. Chemistry of buprestins A and B. Bitter principles of jewel beetles (Coleoptera: Buprestidae). *Austral. J. Chem.* 38: 197–206.
- Bünnige, M. and M. Hilker. 1999. Larval exocrine glands in the galerucine *Agelastica alni* L. (Coleoptera: Chrysomelidae): their morphology and possible functions. *Chemoecology* 9: 55–62.
- Bünnige, M. and M. Hilker. 2005. Do “glanduliferous” larvae of Galerucinae (Coleoptera: Chrysomelidae) possess defensive glands? A scanning electron microscopic study. *Zoomorphology* 124: 111–119.
- Bünnige, M., M. Hilker and S. Dobler. 2008. Convergent evolution of chemical defence in Galerucine larvae. *Biol. J. Linn. Soc.* 93: 165–175.
- Buston, H.W. 1933. Note on the chemical nature from the webs of larvae of *Platyura* and *Ceroplastus*. *Trans. Roy. Entomol. Soc. Lond.* 81: 90–92.
- Callow, R.K., A.R. Greenway and D.C. Griffiths. 1973. Chemistry of the secretion from the cornicles of various species of aphids. *J. Insect Physiol.* 19: 737–748.
- Carlberg, U. 1986. Chemical defence in *Sipylodea sipylus* (Westwood) (Insecta: Phasmida). *Zool. Anz.* 217: 31–38.
- Carrijo-Carvalho, L.C. and A.M. Chudzinski-Tavassi. 2007. The venom of the *Lonomia* caterpillar: An overview. *Toxicon* 49: 741–757.
- Carver, M. 1991. Secretory spines in immatures of *Aleurocanthus* Quaintance and Baker (Hemiptera: Aleyrodidae). *J. Austral. Entomol. Soc.* 30: 265–266.
- Chauhan, K.R., V. Levi, Q.H. Zhang and J.R. Aldrich. 2007. Female goldeneyed lacewings (Neuroptera: Chrysopidae) approach but seldom enter traps baited with the male-produced compound iridodial. *J. Econ. Entomol.* 100: 1751–1755.
- Cherniack, E.P. 2010. Bugs as drugs, Part 1: Insects. The “new” alternative medicine for the 21st century? *Altern. Med. Rev.* 15: 124–135.
- Chow, Y.S. and Y.M. Lin. 1986. Actinidine, a defensive secretion of stick insect, *Megacrania alpheus* Westwood (Orthoptera: Phasmatidae). *J. Entomol. Sci.* 21: 97–101.
- Codella, S.G.J. and K.F. Raffa. 1993. Defense strategies of folivorous sawflies. pp. 261–294. *In*: M.R. Wagner and K.F. Raffa (eds.). *Sawfly Life History Adaptations to Woody Plants*. Academic Press, San Diego.
- Cortez, V., M.E. Favila, J.R. Verdu and A.J. Ortiz. 2012. Behavioral and antennal electrophysiological responses of a predator ant to the pygidial gland secretions of two species of neotropical dung-roller beetles. *Chemoecology* 22: 29–38.

- Cragg, G.M., D.G.I. Kingston and D.J. Newman (eds.). 2012. Anticancer Agents from Natural Products, 2nd Ed. CRC Press, Boca Raton.
- Cranston, P.S. 1995. Medical Significance. pp. 365–384. *In*: P. Armitage, P.S. Cranston, L.C.V. Pinder (eds.). The Chironomidae. Chapman and Hall, London.
- Daly, N.L., A.R. Atkins and R. Smith. 1993. Solution structure of the toxic octapeptide, lophyrotomin. *Int. J. Pept. Protein Res.* 42: 366–371.
- Dathe, H.H. 2003. Wirbellose Tiere 5. Teil Insecta (2. Aufl.). Lehrbuch der Speziellen Zoologie. Spektrum, Heidelberg.
- Darling, D.C., F.C. Schroeder, J. Meinwald, M. Eisner and T. Eisner. 2001. Production of cyanogenic secretion by a thyrnid caterpillar (*Calindoea trifascialis*, Thyrnidae, Lepidoptera). *Naturwissenschaften* 88: 306–309.
- Davies, N.W. and J.L. Madden. 1985. Mandibular gland secretion of two parasitoid wasps (Hymenoptera: Ichneumonidae), *J. Chem. Ecol.* 11: 1115–1127.
- Dazzini Valcurone, M. and M. Pavan. 1978. Scent glands and defensive secretions of Rhynchota. *Publicazioni Dell'Istituto Di Entomologia Dell'Universita Di Pavia* 5: 1–46.
- De Facci, M., H.-L. Wang, J.K. Yuvarai, I.A.N. Dublon, G.P. Svensson, T.W. Chapman and O. Anderbrant. 2014. Chemical composition of anal droplets of the eusocial gall-inducing thrips *Kladothrips intermedius*. *Chemoecology* 24: 85–94.
- Degenkolb, T., R.A. Düring and A. Vilcinskas. 2011. Secondary metabolites released by the burring beetle *Nicrophorus vespilloides*: chemical analyses and possible ecological functions. *J. Chem. Ecol.* 37: 724–735.
- Dekker, M. 1984. Biology and venoms of Lepidoptera. pp. 291–330. *In*: A.T. Tu (ed.). Handbook of Natural Toxins, Vol. 2. M. Dekker, New York.
- Del Campo, M.L., J.T. King and M.R. Gronquist. 2011. Defensive and chemical characterization of the froth produced by the cecropid *Aphrophora cribrata*. *Chemoecology* 21: 1–8.
- Delgado Quiroz, A. 1978. Venoms of Lepidoptera. pp. 555–612. *In*: S. Bettini (ed.). Arthropod Venoms. Springer, Berlin.
- Deml, R. 2001. Secondary compounds in caterpillars of four moth families (Noctuoidea, Bombycoidea) are partly identical. *Nota lepid.* 24: 65–76.
- Deml, R. 2003. Pyrrolidonyl and Pyridyl Alkaloids in *Lymantria dispar*. *Z. Naturforsch.* 58c: 860–866.
- Deml, R. and K. Dettner. 1993. Biogenic amines and phenolics characterize the defensive secreticon of saturniid caterpillars (Lepidoptera: Saturniidae): a comparative study. *J. Comp. Physiol. B* 163: 123–132.
- Deml, R. and K. Dettner. 1996. "Balloon hairs" of gipsy moth larvae (Lep., Lymantriidae): morphology and comparative chemistry. *Comp. Biochem. Physiol.* 112B: 673–681.
- Deml, R. and K. Dettner. 1997. Chemical defence of emperor moths and tussock moths (Lepidoptera: Saturniidae, Lymantriidae). *Entomologia Gener.* 21: 225–251.
- Deml, R. and K. Dettner. 2003. Comparative morphology and secretion chemistry of the scoli in caterpillars of *Hyalophora cecropia*. *Naturwissenschaften* 90: 460–463.
- Deml, R. and K. Dettner. 2004. Defensive potential of the colourful scoli and haemolymph from caterpillars of *Hyalophora cecropia* (LINNAEUS 1758) (Lepidoptera: Saturniidae). *Entomol. Z.* 114: 23–26.
- Dettner, K. 1985. Ecological and phylogenetic significance of defensive compounds from pygidial glands of Hydradephaga (Coleoptera). *Proc. Acad. Natl. Sci. Philadelphia* 137: 156–171.
- Dettner, K. 1987. Chemosystematics and evolution of beetle chemical defenses. *Annu. Rev. Entomol.* 32: 17–48.
- Dettner, K. 1993. Defensive secretions and exocrine glands in free-living staphylinid beetles — Their bearing on phylogeny (Coleoptera: Staphylinidae). *Biochem. System. Ecol.* 21: 143–162.
- Dettner, K. 1997. Inter- and intraspecific transfer of toxic insect compound cantharidin. pp. 115–145. *In*: K. Dettner, G. Bauer and W. Völkl (eds.). Vertical Food Web Interactions. Springer, Berlin.

- Dettner, K. 2010. Chemical defense and toxins of lower terrestrial and freshwater animals. pp. 387–410. *In*: L. Mander and H.W. Lui (eds.). *Comprehensive Natural Products II -Chemistry and Biology*, Vol. 4. Elsevier, Oxford.
- Dettner, K. 2011. Potential pharmaceuticals from insects and their co-occurring microorganisms. pp. 95–119. *In*: A. Vilcinskas (ed.). *Insect Biotechnology, Series: Biologically-Inspired Systems*, Vol. 2. Springer, Dordrecht.
- Dettner, K. 2014. Chemical ecology and biochemistry of Dytiscidae. pp. 235–306. *In*: D.A. Yee (ed.). *Ecology, Systematics, and the Natural History of Predaceous Diving Beetles (Coleoptera: Dytiscidae)*. Springer, Berlin.
- Dettner, K. and M. Böhner. 2009. Die Pygidialdrüse der Wassertreter (Coleoptera: Haliplidae): Morphologie, Chemie, Funktion und phylogenetische Bedeutung. *Contr. Nat. Hist.* 12: 437–460.
- Dettner, K., G. Bauer and W. Völkl. 1997. Evolutionary patterns and driving forces in vertical food-web interactions. pp. 337–377. *In*: K. Dettner, G. Bauer and W. Völkl (eds.). *Vertical Food Web Interactions*. Springer Verlag, Berlin.
- Dettner, K., A. Scheuerlein, P. Fabian, S. Schulz and W. Francke. 1996. Chemical defense of giant springtail *Tetrodontophora bielanensis* (WAGA) (Insecta: Collembola). *J. Chem. Ecol.* 22: 1051–1074.
- Deyrup, S.T., L.E. Eckman, E.E. Lucadamo, P.H. McCarthy, J.C. Knapp and J.R. Smedley. 2014. Antipredator activity and endogenous biosynthesis of defensive secretion in larval and pupal *Delphastus catalinae* (Horn) (Coleoptera: Coccinellidae). *Chemoecology* 24: 145–157.
- Dixon, A.F.G. 1997. *Aphid Ecology*, 2nd edition. Springer, Berlin.
- Dossey, A.T. 2010. Insects and their chemical weaponry: New potential for drug discovery. *Nat. Prod. Rep.* 27: 1737–1757.
- Dossey, A.T. 2011. Chemical defenses of insects: A rich resource for chemical biology in the tropics. pp. 27–57. *In*: J.M. Vivanco and T. Weir (eds.). *Chemical Biology of the Tropics – An Interdisciplinary Approach*. Springer, Heidelberg.
- Dossey, A.T., M. Gottardo, J.M. Whitaker, W.R. Roush and A.S. Edison. 2009. Alkyldimethylpyrazines in the defensive spray of *Phyllium westwoodii*: A first for order Phasmatodea. *J. Chem. Ecol.* 35: 861–870.
- Dossey, A.T., J.M. Whitaker, M.C.A. Dancel, R.K. Vander Meer, U.R. Bernier, M. Gottardo and W.R. Roush. 2012. Defensive spiroketals from *Asceles glaber* (Phasmatodea): absolute configuration and effects on ants and mosquitoes. *J. Chem. Ecol.* 38: 1105–1115.
- Dotimas, E.M. and R.C. Hider. 1987. Honeybee venom. *Bee World* 68: 51–70.
- Dougherty, M.J. and J.G.C. Hamilton. 1996. A biologically-active compound from pupae of the sandfly *Lutzomyia longipalpis* (Diptera: Psychodidae) and its possible role in defense. *Bull. Entomol. Res.* 86: 11–16.
- Dowd, P.F. 1992. Insect fungal symbionts: a promising source of detoxifying enzymes. *J. Industr. Microbiol.* 9: 149–161.
- Drilling, K. and K. Dettner. 2010. First insights into the chemical defensive system of the erotyloid beetle, *Tritoma bipustulata*. *Chemoecology* 20: 243–253.
- Drilling, K., K. Dettner and K.-D. Klass. 2013. The distribution and evolution of exocrine compound glands in Erotylinae (Insecta: Coleoptera: Erotylidae). *Ann. Soc. Entomol. France (N.S.)* 49: 36–52.
- Duffield, R.M. 1981. 2-Nonanol in the exocrine secretion of the Nearctic caddisfly *Rhyacophila fuscula* (Walker) (Rhyacophilidae: Trichoptera). *Proc. Entomol. Soc. Wash.* 83: 60–63.
- Duffield, R.M., M.S. Blum, J.B. Wallace, H.-A. Lloyd and F.-E. Regnier. 1977. Chemistry of the defensive secretion of the caddisfly *Pycnopsyche scabripennis* (Trichoptera: Limnephilidae). *J. Chem. Ecol.* 3: 649–656.
- Dumbacher, J.P., A. Wako, S.R. Derrickson, A. Samuelson, T.F. Spande and J.W. Daly. 2004. Melyrid beetles (*Choresine*): A putative source for the batrachotoxin alkaloids found in poison-dart frogs and toxic passerine birds. *Proc. Natl. Acad. Sci. USA* 101: 15857–15860.

- Dyer, H.F.G.L.A. and A.M. Smilanich. 2012. Feeding by lepidopteran larvae is dangerous: A review of caterpillars' chemical, physiological, and behavioral defenses against natural enemies. *Invertebr. Survival J.* 9: 7–34.
- Edwards, J.S. 1966. Defense by smear: supercoiling in the cornicle wax of Aphids. *Nature* 5044: 73–74.
- Ehmke, A., P. Proksch, L. Witte, T. Hartmann and M.B. Isman. 1989. Fate of ingested pyrrolizidine alkaloid N-oxide in the grasshopper *Melanoplus sanguinipes*. *Naturwissenschaften* 76: 27–29.
- Eisner, T. 1960. Defense mechanisms of arthropods. II. The chemical and mechanical weapons of an earwig. *Psyche* 67: 62–70.
- Eisner, T. 1970. Chemical defense against predation in arthropods. pp. 157–217. *In*: E. Sondheimer and J.B. Simeone (eds.). *Chemical Ecology*. Academic Press, New York.
- Eisner, T. 2003. *For Love of Insects*. Belknap Press of Harvard University Press, Cambridge.
- Eisner, T., R. Ziegler, L. McCormick, M. Eisner, E.R. Hoebeker and J. Meinwald. 1994. Defensive use of an acquired substance (carminic acid) by predaceous insect larvae. *Experientia* 50: 610–615.
- Eisner, T., A.B. Attygalle, W.E. Conner, M. Eisner, E. MacLeod and J. Meinwald. 1996. Chemical egg defense in a green lacewing (*Ceraeochrysa smithi*). *Proc. Natl. Acad. Sci. USA* 93: 3280–3283.
- Eisner, T., M. Eisner and M. Siegler. 2005. *Secret Weapons*. Belknap Press, Cambridge.
- Eisner, T., R.C. Morgan, A.B. Attygalle, S.R. Smedley, K.B. Herath and J. Meinwald. 1997. Defensive production of quinoline by a phasmid insect (*Oreophoetes peruana*). *J. Exp. Biol.* 200: 2493–2500.
- Eisner, T., C. Rossini and M. Eisner. 2000. Chemical defense of an earwig (*Doru taeniatum*). *Chemoecology* 10: 8–87.
- Eisner, T., F.C. Schroeder, N. Snyder, J.B. Grant, D.J. Aneshansley, D. Utterback, J. Meinwald and M. Eisner. 2008. Defensive chemistry of lycid beetles and of mimetic carambycid beetles that feed on them. *Chemoecology* 18: 109–119.
- Epstein, M., S.R. Smedley and T. Eisner. 1994. Sticky integumental coating of a dalcerid caterpillar: a deterrent to ants. *J. Lepidopt. Soc.* 48: 381–386.
- Evans, D.L. and J.O. Schmidt. 1990. *Insect Defenses*. State University of New York Press, Albany.
- Eyal, J., A. Mabud, K.L. Fischbein, J.F. Walter, L.S. Osborne and Z. Landa. 1994. Assessment of *Beauveria bassiana* Nov. EO-1 strain, which produces a red pigment for microbial control. *Appl. Biochem. Biotechnol.* 44: 65–80.
- Farine, J.-P., C. Everaerts, J.-L. Le Quere, E. Semon, R. Henry and R. Brossut. 1997. The defensive secretion of *Eurycotis floridana* (Dictyoptera, Blattidae, Polyzoisteriinae): Chemical identification and evidence of an alarm function. *Insect Biochem. Mol. Biol.* 27: 577–586.
- Farine, J.P., C. Everaerts, D. Abed and R. Brossut. 2000. Production, regeneration and biochemical precursors of the major components of the defensive secretion of *Eurycotis floridana* (Dictyoptera, Polyzoisteriinae). *Insect Biochem. Mol. Biol.* 30: 601–608.
- Farine, J.-P., E. Semon, C. Everaerts, D. Abed, P. Grandcolas and R. Brossut. 2002. Defensive secretion of *Therea petiveriana*: chemical identification and evidence of an alarm function. *J. Chem. Ecol.* 28: 1629–1640.
- Feng, Y., M. Jianqi, L. Zhongren and G. Tianpeng. 1988. A preliminary investigation on the cantharidin resources of Shaanxi province. *Acta Univ. Sept. Occid. Agric.* 16: 23–28.
- Fitzgerald, K.T. and A.A. Flood. 2006. Hymenopteran stings. *Clin. Tech. Small Animal Practice* 21: 194–204.
- Fletcher, M.T. and W. Kitching. 1995. Chemistry of fruit flies. *Chem. Rev.* 95: 789–828.
- Francke, W. and K. Dettner. 2005. Chemical signalling in beetles. *Top. Curr. Chem.* 240: 85–166.
- Francois, J. and R. Dallai. 1986. Les glandes abdominales des Protures. pp. 273–280. *In*: R. Dallai (ed.). 2nd Internat. Seminar on Apterygota. Siena.

- Frankfater, C., M.R. Tellez and M. Slattery. 2009. The scent of alarm: ontogenetic and genetic variation in the osmeterial chemistry of *Papilio glaucus* (Papilionidae) caterpillars. *Chemoecology* 19: 81–96.
- Franzl, S. and C.M. Naumann. 1985. Cuticular cavities: Storage chambers for cyanoglucoside-containing defensive secretions in larvae of a zygaenid moth. *Tissue Cell* 17: 267–278.
- Frenzel, M., K. Dettner, W. Boland and P. Erbes. 1990. Identification and biological significance of 4-methyl-3Z,5-hexadienoic acid produced by males of the gall-forming tephritids *Urophora cardui* (L.) and *Urophora stylata* (Fab.) (Diptera: Tephritidae). *Experientia* 46: 542–547.
- Frenzel, M. and K. Dettner. 1994. Quantitation of cantharidin in canthariphilic ceratopogonids (Diptera: Ceratopogonidae), Anthomyiids (Diptera) and cantharidin-producing Oedemerids (Coleoptera). *J. Chem. Ecol.* 20: 1795–1812.
- Fu, X., F.V. Vencl, O. Nobuyoshi, V.B. Meyer-Rochow, C. Lei and Z. Zhang. 2007. Structure and function of the eversible glands of the aquatic firefly *Luciola leii* (Coleoptera: Lampyridae). *Chemoecology* 17: 117–124.
- Gebhardt, K., J. Schimana, P. Krastel, K. Dettner, J. Rheinheimer, A. Zeeck and H.-P. Fiedler. 2002. Endophenazines A–D, new phenazine antibiotics from the arthropod associated endosymbiont *Streptomyces anulatus*. I. Taxonomy, fermentation, isolation and biological activities. *J. Antibiotics* 55: 794–800.
- Gomez, J., J.F. Barrera, J.C. Rojas, J. Macias-Samano, J.P. Liedo, L. Cruz-Lopez and M.H. Badii. 2005. Volatile compounds released by disturbed females of *Cephalonomia stephanoderis* (Hymenoptera: Bethyilidae): A parasitoid of the coffee berry borer *Hypothenemus hampei* (Coleoptera: Scolytidae). *Florida Entomol.* 88: 180–187.
- Greeney, H.F., L.A. Dyer and A.M. Smilanich. 2012. Feeding by lepidopteran larvae is dangerous: A review of caterpillars' chemical, physiological, morphological and behavioral defenses against natura enemies. *Invertebr. Survival J.* 9: 7–34.
- Gronquist, M., J. Meinwald, T. Eisner and F. Schroeder. 2005. Exploring uncharted terrain in nature's structure space using capillary NMR spectroscopy: 13 steroids from 50 fireflies. *J. Am. Chem. Soc.* 127: 10810–10811.
- Gronquist, M. and F.C. Schroeder. 2010. Insect natural products. pp. 67–107. *In: L. Mander and H.W. Liu (eds.). Comprehensive Natural Products II Chemistry Biology, Vol. 2. Elsevier, Amsterdam.*
- Grzeschik, K.H. 1969. On the systematics, biology and ethology of *Eugaster* SERVILLE (Orthoptera, Tettigoniidae). *Forma et Functio* 1: 111–144.
- Güsten, R. 1996. A review of epidermal glands in the order Neuroptera (Insecta). pp. 129–146. *In: M. Canard, H. Aspöck and M.W. Mansell (eds.). Pure and Applied Research in Neuropterology. Proc. 5th Int. Symp. Neuropterol. Cairo, Egypt, 1994.*
- Güsten, R. 1998. The morphology of the metathoracic gland system in the Myrmeleontidae (Neuroptera): a preliminary overview. *Acta Zool. Fennica* 209: 121–127.
- Güsten, R. and K. Dettner. 1992. The prothoracic gland of the Chrysopidae (Neuropteroidea: Planipennia). *Proc. 4. Europ. Congr. Entomol., XIII. SIEEC, Gödöllő* 60–65.
- Guilford, T., C. Nicol, M. Rothschild and B. Moore. 1987. The biological roles of pyrazines: evidence for a warning odour function. *Biol. J. Linn. Soc.* 31: 113–128.
- Haeder, S., R. Wirth, H. Herz and D. Spiteller. 2009. Candicidin-producing *Streptomyces* support leaf-cutting ants to protect their fungus garden against the pathogenic fungus *Escovopsis*. *Proc. Natl. Acad. Sci. USA* 106: 4742–4746.
- Haga, K., T. Suzuki, S. Kodama and Y. Kuwahara. 1989. Secretion of thrips, III. Secretion of acid-emitting thrips, *Holothrips japonicus* (Thysanoptera: Phlaeothripidae). *Appl. Entomol. Zool.* 24: 242–244.
- Hallberg, E. and G. Poppy. 2003. Exocrine Glands: Chemical communication and chemical defense. pp. 361–375. *In: Handbook of Zoology, Lepidoptera Vol. II, De Gruyter, Berlin.*
- Hansen, J.A., E.C. Bernard and J.K. Moulton. 2010. A defensive behaviour of *Acerentulus confinis* (Berlese) (Protura, Acerentomidae). *Proc. Entomol. Soc. Wash.* 112: 43–46.

- Hatle, J.D. and S.G. Faragher. 1998. Slow movement increases the survivorship of a chemically defended grasshopper in predatory encounters. *Oecologia* 115: 260–267.
- Helson, J.E., L.C. Todd, T. Johns, A. Aiello and D.M. Windsor. 2009. Ecological and evolutionary bioprospecting: using aposematic insects as guides to rainforest plants active against disease. *Front. Ecol. Environm.* 7: 130–134.
- Hemp, C. and K. Dettner. 2001. Compilation of canthariphilous insects. *Beitr. Entomol.* 51: 231–245.
- Hermann, H.R. 1984. *Defensive Mechanisms in Social Insects*. Praeger, New York.
- Hilker, M. and T. Meiners (eds.). 2002. *Chemoecology of Insect Eggs and Egg Deposition*. Blackwell, Berlin.
- Hings, C.F. and J.R. Byers. 1975. A New glandular organ in some toxic caterpillars. *Experientia* 31: 965–967.
- Hinton, H.E. 1981. *Biology of Insect Eggs*, Vol. 1–3, Pergamon, Oxford.
- Hoffman, D.R. 2010. Ant venoms. *Curr. Opin. Allergy Clin. Immunol.* 10: 1–5.
- Holliday, A.E., N.J. Holliday, T.M. Mattingly and K.N. Naccarato. 2012. Defensive secretion of the carabid beetle *Chlaenius cordicollis*: chemical components and their geographic patterns of variation. *J. Chem. Ecol.* 38: 278–286.
- Houston, T.F. 2007. Observations on the biology and immature stages of the sandgroper *Cylindraustralia kochii* (Saussure), with notes on some congeners (Orthoptera: Cylindrauchetidae). *Rec. West. Austral. Museum* 23: 219–234.
- Howard R.W. and J.C. Lord. 2003. Cuticular lipids of the stored food pest, *Liposcelis bostrychophila*: hydrocarbons, aldehydes, fatty acids and fatty amides. *J. Chem. Ecol.* 29: 597–609.
- Howard, D.F., M.S. Blum and H.M. Fales. 1983. Defense in thrips: forbidden fruitiness of a lactone. *Science* 220: 335–336.
- Howard, D.F., M.S. Blum, T.H. Jones, H.M. Fales and M.D. Tomalski. 1987. Defensive function and chemistry of the anal exudate of the Cuban laurel thrips *Gynaikothrips ficorum* (MARCHAL). *Phytophaga* 1: 163–170.
- Howse, P.E. 1984. Sociochemicals of termites. pp. 475–519. *In*: W.J. Bell and R.T. Cardé (eds.) *Chemical Ecology of Insects*. Chapman and Hall, London.
- Ivanov, V.D. and S.I. Melnitsky. 1999. The structure of the sternal pheromone glands in caddis flies (Trichoptera). *Entomologicheskoe Obozrenie* 78: 505–526.
- Ivarsson, P., B.-I. Henrikson and J.A.E. Stenson. 1996. Volatile substances in the pygidial secretion of gyrinid beetles (Coleoptera: Gyrinidae). *Chemoecology* 7: 191–193.
- Janetschek, H. 1970. Protura (Beintastler). pp. 1–72. *In*: J.G. Helmcke, D. Stark and H. Wermuth (eds.). *Handbuch der Zoologie*, Vol. 4. De Gruyter, Berlin.
- Johnson, J.B. and K.S. Hagen. 1981. A neuropteran larva uses an allomone to attack termites. *Nature* 289: 506–507.
- Juanjie, T., Z. Jouwei, W. Shuyong, D. Zengji and Z. Xhuanxian. 1995. Investigation on the natural resources and utilization of the Chinese medicinal beetles—Meloidae. *Acta Entomol. Sin.* 38: 324–331.
- Kadavy, D.R., J.M. Hornby, T. Haverkost and K.W. Nickerson. 2000. Natural antibiotic resistance of bacteria isolated from larvae of the oil fly *Helaeomyia petrolei*. *Appl. Environm. Microbiol.* 4615–4619.
- Kador, M., M.A. Horn and K. Dettner. 2011. Novel oligonucleotide probes for *in situ* detection of pederin-producing endosymbionts of *Paederus riparius* rove beetles (Coleoptera: Staphylinidae). *FEMS Microbiol. Lett.* 319: 73–81.
- Kahan, D. 1964. The toxic effect of the bite and the proteolytic activity of the saliva and stomach contents of the robber flies (Diptera Asilidae). *Israel J. Zool.* 13: 47–57.
- Kaltenbach, A. 1978. Mecoptera (Schnabelhafte, Schnabelfliegen). pp. 1–111. *In*: J.-G. Helmcke, D. Starck and H. Wermuth (eds.). *Handbuch der Zoologie*, IV. Band, 2. Hälfte (Insecta) (M. Beier, ed.) 2. Teil Spezielles, Band 28. De Gruyter, Berlin.
- Kaltenpoth, M. and T. Engl. 2014. Defensive microbial symbionts in Hymenoptera. *Functional Ecol.* 28: 315–327.

- Kastin, A. 2013. Handbook of Biologically Active Peptides, 2nd edition. Elsevier, San Diego.
- Keefover-Ring, K. 2013. Making scents of defense: do fecal shields and herbivore-caused volatiles match host plant chemical profiles? *Chemoecology* 23: 1–11.
- Keeling, C.I., E. Plettner and K.N. Slessor. 2004. Hymenopteran semiochemicals. pp. 133–177. *In*: S. Schulz (ed.). *The Chemistry of Pheromones and other Semiochemicals*, Vol. I. Springer, Berlin.
- Kellner, R.L.L. and K. Dettner. 1996. Differential efficacy of toxic pederin in deterring potential arthropod predators of *Paederus* offspring (Coleoptera: Staphylinidae). *Oecologia* 107: 293–300.
- Kenny, P.T.M., S.Y. Tamura, A. Fredenhagen, Y. Naya, K. Nakanishi, K. Nishiyama, M. Suguira, H. Kita and H. Komura. 1989. Symbiotic microorganisms of insects: A potential new source for biologically active substances. *Pest. Sci.* 27: 117–131.
- King, A.G. and J. Meinwald. 1996. Review of the defensive chemistry of coccinellids. *Chem. Rev.* 96: 1105–1122.
- King, T.P. and M.D. Spangfort. 2000. Structure and biology of stinging insect venom allergens. *Int. Arch. Allergy Immunol.* 123: 99–106.
- Klotz, J.H., S. Klotz and J.L. Pinnas. 2009. Animal bites and stings with anaphylactic potential. *J. Emerg. Med.* 36: 148–156.
- Kozlov, M.V. and E.L. Zvereva. 1999. A failed attempt to demonstrate pheromone communication in archaic moths of the genus *Sabatinca* Walker (Lepidoptera, Micropterigidae). *Ecol. Lett.* 2: 215–218.
- Kroiss, J., M. Kaltenpoth, B. Schneider, M.-G. Schwinger, C. Hertweck, R.K. Maddula, E. Strohm and A. Svatoš. 2010. Symbiotic streptomycetes provide antibiotic combination prophylaxis for wasp offspring. *Nature Chem. Biol.* 6: 261–263.
- Kutalek, R. and A. Kassa. 2005. The use of Gyrinids and Dytiscids for stimulating breast growth in East Africa. *J. Ethnobiol.* 25: 115–128.
- LaMunyon, C.W. and P.A. Adams. 1987. Use and effect of an anal defensive secretion in larval Chrysopidae (Neuroptera). *Ann. Entomol. Soc. Am.* 80: 804–808.
- Lang, C., K. Seifert and K. Dettner. 2012. Skimming behaviour and spreading potential of *Stenus* species and *Dianous coerulescens* (Coleoptera: Staphylinidae). *Naturwissenschaften* 99: 937–947.
- Laurent, P., J.C. Braekman and D. Daloz. 2005. Insect chemical defense. *Top. Curr. Chem.* 240: 167–230.
- Leclercq, S., J.C. Braekman, D. Daloz and J.M. Pasteels. 2000. The defensive chemistry of ants. *Progr. Chem. Org. Nat. Prod.* 79: 115–229.
- Lehane, M.J. 2005. *The Biology of Blood-sucking in Insects*. 2nd edition, Cambridge Univ. Press, Cambridge.
- Levick, N.R., J.O. Schmidt, J. Harrison, G.S. Smith and K.D. Winkel. 2000. Review of bee and wasp sting injuries in Australia and the USA. pp. 437–447. *In*: A.D. Austin, M. Dowton (eds.). *Hymenoptera, Evolution, Biodiversity and Biological Control*. CSIRO-Publishing, Melbourne.
- Li, J., S. Lehmann, B. Weißbecker, I.O. Naharro, S. Schütz, G. Joop and E.A. Wimmer. 2013. Odoriferous defensive stink gland transcriptome to identify novel genes necessary for quinone synthesis in the red flour beetle *Tribolium castaneum*. *Plos Genetics* 9: 1–18.
- Lindström, L., C. Rowe and T. Guilford. 2001. Pyrazine odour makes visually conspicuous prey aversive. *Proc. Roy. Soc. Lond. Serie B* 268: 159–162.
- Löfstedt, C., B.S. Hansson, E. Petterson, P. Valeur and A. Richards. 1994. Pheromonal secretions from glands on the 5th abdominal sternite of hydroptychid and rhyacophilid caddisflies (Trichoptera). *J. Chem. Ecol.* 20: 153–170.
- Löfstedt, C., J. Bergmann, W. Francke, E. Jirle, B.S. Hansson and V.D. Ivanov. 2008. Identification of a sexpheromone produced by sternal glands in females of the caddisfly *Molanna angustata* Curtis. *J. Chem. Ecol.* 34: 220–228.
- Lokensgard, J., R.L. Smith, T. Eisner and J. Meinwald. 1993. Pregnanes from defensive glands of a belostomatid bug. *Experientia* 49: 175–176.

- Lokeshwari, R.K. and T. Shantibala. 2010. A review on the fascinating world of insect resources: Reasons for thoughts. *Psyche* 1–11.
- Lusebrink, I., D. Burkhardt, T. Gedig, K. Dettner, A. Mosandl and K. Seifert. 2007. Intrageneric differences in the four stereoisomers of stenusine in the rove beetles genus, *Stenus* (Coleoptera, Staphylinidae). *Naturwissenschaften* 94: 143–147.
- Lusebrink, I., K. Dettner, A. Schierling, T. Müller, C. Daolio, B. Schneider, J. Schmidt and K. Seifert. 2009. Newpyridine alkaloids from rove beetles from the Genus *Stenus* (Coleoptera: Staphylinidae). *Zeitschr. Naturforsch.* 64c: 271–278.
- Marcussen, B.M., J.A. Axelsen and S. Toft. 1999. The value of two Collembola species as food for a linyphiid spider. *Entomol. Exp. Appl.* 92: 29–36.
- Matsuda, K., H. Suzuki, F. Nakanishi, K. Shio, K. Komai and K. Nishimura. 1995. Purification and characterization of a paralytic polypeptide from larvae of *Myrmeleon bore*. *Biochem. Biophys. Res. Commun.* 215: 167–171.
- Mattiacci, L., S.B. Vinson, H.J. Williams, J.R. Aldrich and F. Bin. 1993. A long-range attractant kairomone for egg parasitoid *Trissolcus basalus*, isolated from defensive secretion of its host, *Nezara viridula*. *J. Chem. Ecol.* 19: 1167–1181.
- Mayr, L. 1975. Untersuchungen zur Funktion der Speicheldrüsen räuberischer Gallmückenlarven (*Aphidoletes aphidimyza* Rond.) *Z. ang. Ent.* 77: 270–273.
- McLeod, M.P., A.T. Dossey and M.K. Ahmed. 2007. Application of attenuated total reflection infrared spectroscopy in the study of *Peruphasma schultei* defensive secretion. *Spectroscopy* 21: 169–176.
- Mebs, D. 2010. Gifftiere, 3. Ed. Wissenschaftliche Verlagsgesellschaft, Stuttgart.
- Meinwald, J., G.M. Happ, J. Labours and T. Eisner. 1966. Cyclopentanoid terpene biosynthesis in a phasmid insect and in catmint. *Science* 151: 79–80.
- Meixner, J. 1935. Achte Überordnung der Pterygogenea: Coleopteroidea 1037–1382, Textfig. pp. 1157–1423. *In: Th. Krumbach* (Herausgeber). *Handbuch der Zoologie*, gegr. v. W. Kükenthal, 4. Band, 2. Hälfte, 1. Teil, Insecta 2. Walter de Gruyter & Co., Berlin.
- Mello, M.L.S., E.R. Pimentel, A.T. Yamada and A. Storopoli-Neto. 1987. Composition and structure of the froth of the spittlebug, *Deois* sp. *Insect Biochem.* 17: 49–502.
- Messer, C., K. Dettner, S. Schulz and W. Francke. 1999. Phenolic compounds in *Neanura muscorum* (Collembola, Neanuridae) and the role of 1,3-dimethoxybenzene as an alarm substance. *Pedobiologia* 43: 174–182.
- Messer, C., J. Walther, K. Dettner and S. Schulz. 2000. Chemical deterrents in podurid Collembola. *Pedobiologia* 44: 210–220.
- Millar, J.G. 2005. Pheromones of true bugs. pp. 37–84. *In: S. Schulz* (ed.). *The Chemistry of Pheromones and Other Semiochemicals*, Vol. II. Springer, Berlin.
- Moayeri, H.R.S., A. Rasekh and A. Enkegaard. 2014. Influence of cornicle droplet secretions of the cabbage aphid, *Brevicoryne brassicae*, on parasitism behavior of naïve and experienced *Diaeretiella rapae*. *Insect Sci.* 21: 56–64.
- Moore, B.P. and W.V. Brown. 1985. The buprestins: bitter principles of jewel beetles (Coleoptera: Buprestidae). *J. Austral. Entomol. Soc.* 24: 81–85.
- Moore, K.A. and D.D. Williams. 1990. Novel strategies in the complex defensive repertoire of a stonefly (*Pteronarcys dorsata*) nymph. *Oikos* 57: 49–56.
- Morgan, E.D. 2004. *Biosynthesis in Insects*. Royal Society of Chemistry, Cambridge.
- Moritz, G. 2006. Thripse. pp. 1–384. Westarp, Hohenwarsleben.
- Moriya, N. 1989. Morphology and histology of the scent glands of the pigmy mole cricket *Tridactylus japonicus* DE HAAN (Orthoptera: Tridactylidae). *Appl. Entomol. Zool.* 24: 161–168.
- Moriya, N. and T. Ichinose. 1988. Function of the scent from the pigmy mole cricket *Tridactylus japonicus* DE HAAN (Orthoptera: Tridactylidae). *Appl. Entomol. Zool.* 23: 321–328.
- Mosey, R.A. and P.E. Floreancig. 2012. Isolation, biological activity, synthesis, and medicinal chemistry of the pederin/mycalamide family of natural products. *Nat. Prod. Report* 29: 980–995.

- Moskowitz, D.P. 2002. An unusual interaction between a banded hairstreak butterfly *Satyrium calanus* (Lycaenidae) and a stink bug *Banasa dimiata* (Pentatomidae). *Entomol. News* 113: 183–186.
- Müller, T., M. Göhl, I. Lusebrink, K. Dettner and K. Seifert. 2012. Cicindeloline from *Stenus cicindeloides*—isolation, structure elucidation and total synthesis. *Eur. J. Org. Chem.* 12: 2323–2330.
- Müller, U.R. 1988. *Insektenstichallergie*. Gustav Fischer, Stuttgart.
- Munir, E., J.J. Yoon, T. Tokimatsu, T. Hattori and M. Shimada. 2001. A physiological role for oxalic acid biosynthesis in the wood-rotting basidiomycet *Formitopsis palustris*. *Proc. Natl. Acad. Sci. USA* 98: 11126–11130.
- Nakatani, T., E. Nishimura and N. Noda. 2006. Two isoindoline alkaloids from the crude drug, the ant lion (the larvae of Myrmeleontidae species). *J. Nat. Med.* 60: 261–263.
- Nelson, D.R., T.P. Freeman, J.S. Buckner, K.A. Hoelmer, C.G. Jackson and J.R. Hagler. 2003. Characterization of the cuticular surface wax pores and the waxy particles of the dustywing, *Semidalis flinti* (Neuroptera: Coniopterygidae). *Comp. Biochem. Mol. Biol.* 136: 343–356.
- Nickle, D.A., J.L. Castner, S.R. Smedley, A.B. Attygalle, J. Meinwald and T. Eisner. 1996. Glandular pyrrazine emission by a tropical Katydid: an example of chemical aposematism? (Orthoptera: Tettigoniidae: Copiphorinae: *Vestria* Stål). *J. Orthopt. Res.* 5: 221–223.
- Nilsson, E. and G. Bengtsson. 2004. Endogenous free fatty acids repel and attract Collembola. *J. Chem. Ecol.* 30: 1431–1433.
- Nishida, R. 2002. Sequestration of defensive substances from plants by Lepidoptera. *Annu. Rev. Entomol.* 47: 57–92.
- Nishiwaki, H., K. Ito, K. Otsuki, H. Yamamoto, K. Komai and K. Matsuda. 2004. Purification and functional characterization of insecticidal sphingomyelinase C produced by *Bacillus cereus*. *Eur. J. Biochem.* 271: 601–606.
- Nishiwaki, H., K. Nakashima, C. Ishida, T. Kawamura and K. Matsuda. 2007. Cloning, functional characterization, and mode of action of a novel insecticidal pore-forming toxin, sphaericolysin, produced by *Bacillus sphaericus*. *Appl. Environ. Microbiol.* 73: 340–3411.
- Numata, A. and T. Ibuka. 1987. Alkaloids from ants and other insects. *The Alkaloids* 31: 193–315.
- Oba, Y., M.A. Branham and T. Fukatsu. 2011. The terrestrial bioluminescent animals of Japan. *Zool. Sci.* 28: 771–789.
- O'Connell, T.J. and N.Z. Reagle. 2002. Is the chemical defense of *Eurycotis floridana* a deterrent to small mammal predators? *Florida Sci.* 65: 245–249.
- Ohta, M., F. Matsuura, G. Henderson and R.A. Laine. 2007. Novel free ceramides as components of the soldier defense gland of the Formosan subterranean termite (*Coptotermes formosanus*). *J. Lip. Res.* 48: 656–664.
- Opitz, S.E.W. and C. Müller. 2009. Plant chemistry and insect sequestration. *Chemoecology* 19: 117–154.
- Pankewitz, F. and M. Hilker. 2006. Defensive components in insect eggs: are anthraquinones produced during egg development? *J. Chem. Ecol.* 32: 2067–2072.
- Pankewitz, F. and M. Hilker. 2008. Polyketides in insects: ecological role of these widespread chemicals and evolutionary aspects of their biogenesis. *Biol. Rev.* 83: 209–226.
- Pankewitz, F., A. Zöllmer, Y. Gräser and M. Hilker. 2007a. Anthraquinones as defensive compounds in eggs of Galerucini leaf beetles: biosynthesis by the beetles? *Arch. Insect Biochem. Physiol.* 66: 98–108.
- Pankewitz, F., A. Zöllmer, M. Hilker and Y. Gräser. 2007b. Presence of *Wolbachia* in insect eggs containing antimicrobially active anthraquinones. *Microbial Ecol.* 54: 713–721.
- Parfin, S. 1952. Notes on the bionomics of *Corydalis cornutus* (Linné), *Chauliodes rastricornis* Rambur, *C. pectinicornis* (Linné) and *Neohermes* sp. *Am. Midland Naturalist* 47: 426–434.

- Parker, S.P. 1982. Synopsis and Classification of Living Organisms, Vol. 2. McGraw-Hill, New York.
- Pasteels, J.M., D. Daloz, J.-C. de Biseau, A. Termonia and D.M. Windsor. 2004. Patterns in host-plant association and defensive toxins produced by neotropical chrysomeline beetles. pp. 669–676. *In*: P. Jolivet, J.A. Santiago-Blay and M. Schmitt (eds.). New Developments in the Biology of Chrysomelidae. SPB Academic Publishing, The Hague.
- Pavan, M. 1975. Gli iridoidi negli insetti. *Pubblicaciones Instituto Entomologia Agraria Universita di Pavia* 2: 1–49.
- Pavan, M. and M. Valcurone Dazzini. 1976. Sostanze di difesa dei lepidotteri. *Pubblicaciones Instituto Entomologia Agraria Universita di Pavia* 3: 1–23
- Peck, D.C. 2000. Reflex bleeding in froghoppers (Homoptera: Cercopidae): variation on behavior and taxonomic distribution. *Ann. Entomol. Soc. Am.* 93: 1186–1194.
- Pemberton, R.W. 1999. Insects and other arthropods used as drugs in Korean traditional medicine. *J. Ethnopharmacol.* 65: 207–216.
- Petre, C.A., C. Detrain and J.-L. Boevé. 2007. Anti-predator defence mechanisms in sawfly larvae of *Arge* (Hymenoptera, Argidae). *J. Insect Physiol.* 53: 668–675.
- Pfander, I. and J. Zettel. 2004. Chemical communication in *Ceratophysella sigillata* (Collembola: Hypogastruridae): intraspecific reaction to alarm substances. *Pedobiologia* 48: 575–580.
- Pickett, J.A., R.K. Allemann and M.A. Birkett. 2013. The semiochemistry of aphids. *Nat. Prod. Rep.* 30: 1277–1283.
- Piek, T. (ed.). 1986. Venoms of the Hymenoptera-Biochemical, Pharmacological and Behavioural Aspects. Academic Press, London.
- Pietra, F. 2002. Biodiversity and Natural Product Diversity. Pergamon Press, Amsterdam.
- Plachter, H. 1979. Zur Kenntnis der Präimaginalstadien der Pilzmücken. Teil I: Gespinnstbau. *Zool. Jahrb. Anat.* 101: 168–266.
- Polanowski, A., M.S. Blum, D.W. Whitman and J. Travis. 1997. Proteinase inhibitors in the nonvenomous defensive secretion of grasshoppers: antiproteolytic range and possible significance. *Comp. Biochem. Physiol.* 117B: 525–529.
- Porco, D. and L. Deharveng. 2007. 1,3-Dimethoxybenzene, a chemotaxonomic marker for the Neanurinae subfamily (Collembola). *Biochem. Syst. Ecol.* 35: 160–161.
- Preston-Mafham, K. 1990. Grasshoppers and Mantids of the World. Facts on File, New York.
- Prestwich, G.D. 1983. Chemical systematics of termite exocrine secretions. *Annu. Rev. Ecol. Syst.* 14: 287–311.
- Prestwich, G.D. 1984. Defense mechanisms of termites. *Annu. Rev. Entomol.* 29: 201–232.
- Prieto, J.M., U. Schaffner, A. Barker, A. Braca, T. Siciliano and J.-L. Boevé. 2007. Sequestration of furostanol saponins by *Monophasma* sawfly larvae. *J. Chem. Ecol.* 33: 513–524.
- Purrington, F.F., P.A. Kendall, J.E. Bater and B.R. Stinner. 1991. Alarm pheromone in a gregarious poduromorph collembolan (Collembola: Hypogastruridae). *Great Lakes Entomol.* 24: 75–78.
- Quennedey, A. 1984. Morphology and ultrastructure of termite defense glands. pp. 151–200. *In*: H.R. Hermann (ed.). *Defensive Mechanisms in Social Insects*. Praeger, New York.
- Quicke, D.L.J. 1997. Parasitic Wasps. Chapman and Hall, London.
- Redborg, K.E. 1983. A mantispid larva can preserve its spider egg prey: evidence for an aggressive allomone. *Oecologia* 58: 230–231.
- Reyes-Garcia, L., M. Fernando Flores and J. Bergmann. 2011. Biological activity of the larval secretion of *Chilecomadia valdiviana*. *J. Chem. Ecol.* 37: 1137–1142.
- Richard, F.L. and D.K. Ledford. 2014. Allergens and Allergen Immunotherapy, 5th edition. CRC Press, Taylor and Francis, Boca Raton.
- Ross, G.N., H.M. Fales, H.A. Lloyd, T. Jones, E.A. Sokoloski, K. Marshall-Batty and M.S. Blum. 2001. Novel chemistry of abdominal defensive glands of nymphalid butterfly *Agraulis vanillae*. *J. Chem. Ecol.* 27: 1219–1228.
- Roth, L.M. and D.W. Alsop. 1978. Toxins of Blattaria. pp. 465–487. *In*: S. Bettini (ed.). *Handbook of Experimental Pharmacology*, Vol. 48. Springer, Berlin.

- Rotheray, G.E. 1986. Colour, shape and defence in aphidophagous syrphid larvae (Diptera). *Zool. J. Linn. Soc.* 88: 201–216.
- Rotschild, M. 1985. British aposematic Lepidoptera. pp. 9–62. In: J. Heath and A.M. Emmet (eds.). *The Moths and Butterflies of Great Britain and Ireland*. Harley, Essex.
- Ryczek, S., K. Dettner and C. Unverzagt. 2009. Synthesis of buprestins D, E, F, G and H; structural confirmation and biological testing of acyl glucosides from jewel beetles (Coleoptera: Buprestidae). *Bioorg. Med. Chem.* 17: 1187–1192.
- Sahayaraj, K. and A. Vinothkanna. 2011. Insecticidal activity of venomous saliva from *Rhynocoris fuscipes* (Reduviidae) against *Spodoptera litura* and *Helicoverpa armigera* by microinjection and oral administration. *J. Ven. Anim. Toxins including Tropical Diseases* 17: 486–490.
- Schaefer, C.W. and A.R. Panizzi (eds.). 2000. *Heteroptera of Economic Importance*. CRC Press, Boca Raton.
- Schal, C., J. Fraser and W.J. Bell. 1982. Disturbance stridulation and chemical defence in nymphs of the tropical cockroach *Megaloblatta blaberooides*. *J. Insect Physiol.* 28: 541–552.
- Schedl, W. 1991. Hymenoptera, Unterordnung Symphyta. *Handbuch der Zoologie; Band IV: Arthropoda: Insecta*. M. Fischer (ed.). de Gruyter, Berlin.
- Schierling, A. and K. Dettner. 2013. The pygidial defense gland system of the Steninae (Coleoptera, Staphylinidae): Morphology, ultrastructure and evolution. *Arthrop. Struct. Dev.* 42: 197–208.
- Schierling, A., K. Seifert, S. Sinterhauf, J.B. Rieß, J.C. Rupprecht and K. Dettner. 2013. The multifunctional pygidial gland secretion of the Steninae (Coleoptera: Staphylinidae): ecological significance and evolution. *Chemoecology* 23: 45–57.
- Schildknecht, H. and K.H. Weis. 1960. VI. Mitteilung über Insektenabwehrstoffe: Zur Kenntnis des Pygidialdrüsen-Sekretes vom gemeinen Ohrwurm, *Forficula auricularia*. *Zeitschr. Naturforschung* 15b: 755–757.
- Schlörke, O., P. Krastel, I. Müller and I. Usón. 2002. Structure and biosynthesis of cetoniacytone A, a cytotoxic aminocarpa sugar produced by an endosymbiotic *Actenomyces*. *J. Antibiot.* 55: 635–642.
- Schmidt, J.O. 1982. Biochemistry of insect venoms. *Annu. Rev. Entomol.* 27: 339–368.
- Schramm, S., K. Dettner and C. Unverzagt. 2006. Chemical and enzymatic synthesis of buprestin A and B-bitter acylglucosides from Australian jewel beetles (Coleoptera: Buprestidae). *Tetrahedron Lett.* 47: 7741–7743.
- Schulz, S. 2004. *The Chemistry of Pheromones and Other Semiochemicals I*. Springer, Berlin.
- Schulz, S. 2005. *The Chemistry of Pheromones and Other Semiochemicals II*. Springer, Berlin.
- Schulz, S., C. Messer and K. Dettner. 1997. Poduran, an unusual tetraterpen from the springtail *Podura aquatica*. *Tetrahedron Lett.* 38: 2077–2080.
- Schwepe, H. 1993. *Handbuch der Naturfarbstoffe*. Ecomed, Landsberg.
- Seiler, C., S. Bradler and R. Koch. 2000. *Phasmiden*. bede-Verlag, Ruhmannsfelden.
- Sloggett, J.J., A. Magro, F.J. Verheggen, J.-L. Hemptinne, W.D. Hutchinson and E.W. Riddick. 2011. The chemical ecology of *Harmonia axyridis*. *BioControl* 56: 643–661.
- Smedley, S.R., F.C. Schroeder, D.B. Weibel, J. Meinwald, K.A. Lafleur, J.A. Renwick, R. Rutowski and T. Eisner. 2002. Mayolenes: Labile defensive lipids from the glandular hairs of a caterpillar (*Pieris rapae*). *Proc. Natl. Acad. Sci. USA* 99: 6822–6827.
- Smith, E.L. 1970. Biology and structure of the Dobsonfly, *Neohermes californicus* (Walker) (Megaloptera: Corydalidae). *Pan-Pacific Entomol.* 46: 142–150.
- Smith, R.M., J.J. Brophy, G.W.K. Cavill and N.W. Davies. 1979. Iridodials and nepetalactone in the defensive secretion of coconut stick insects *Graeffea crouani*. *J. Chem. Ecol.* 5: 727–735.
- Snook, M.E., M.S. Blum, D.W. Whitman, R.F. Arrendale, C.E. Costello and J.S. Harwood. 1993. Caffeoyltartronic acid from catnip (*Nepeta cataria*): A precursor for catechol in lubber grasshoppers (*Romalea guttata*) defensive secretions. *J. Chem. Ecol.* 19: 1957–1966.
- Southcott, R.V. 1991. Injuries from larval Neuroptera. *Med. J. Australia* 154: 329–332.
- Spanton, S.G. and G.D. Prestwich. 1982. Chemical defense and self-defense. *Tetrahedron* 38: 1921–1930.

- Srivastava, S.K., N. Babu and H. Pandey. 2009. Traditional insect bioprospecting—As human food and medicine. *Indian J. Traditional Knowledge* 8: 485–494.
- Staddon, B.W. 1979. The scent glands of Heteroptera. *Adv. Insect Physiol.* 14: 351–418.
- Stocks, I. 2008. Reflex bleeding (Autohemorrhage). pp. 3132–3139. *In: J.L. Capinera (ed.). Encyclopedia of Entomology*, 2nd ed. Springer, Berlin.
- Stransky, K., M. Psoky and M. Streibl. 1986. Lipid compounds from the extract of springtail *Tetradontophora bielaniensis* (Waga). *Collect. Czech Chem. Commun.* 51: 948–955.
- Suzuki, T., K. Haga and Y. Kuwahara. 1986. Anal secretion of thrips. I. Identification of perillene from *Leeuwenia pasanii* (Thysanoptera: Phlaeothripidae). *Appl. Entomol. Zool.* 21: 461–466.
- Suzuki, T., K. Haga, S. Kodama, K. Watanabe and Y. Kuwahara. 1988. Secretion of thrips, II. Secretion of the three gall-inhabiting thrips (Thysanoptera: Phlaeothripidae). *Appl. Entomol. Zool.* 23: 291–297.
- Suzuki, T., K. Haga, W.S. Leal, S. Kodama and Y. Kuwahara. 1989. Secretion of Thrips, IV: Identification of β -Acaridial from Three Gall-Forming Thrips (Thysanoptera: Phlaeothripidae). *Appl. Entomol. Zool.* 24: 222–228.
- Suzuki, T., K. Haga, M. Izuno, S. Matsuiama and Y. Kuwahara. 1993. Secretion of thrips, VII. Identification of 3-butanoyl-4-hydroxy-6-methyl-2H-pyran-2-one from *Holothrips japonicus* and *H. hagai* (Thysanoptera: Phlaeothripidae). *Appl. Entomol. Zool.* 28: 108–112.
- Suzuki, T., K. Haga, T. Tsutsumi and S. Matsuyama. 2004. Analysis of anal secretions from Phlaeothripine thrips. *J. Chem. Ecol.* 30: 409–423.
- Swart, C.C., L.E. Deaton and B.E. Felgenhauer. 2006. The salivary gland and salivary enzymes of the giant waterbugs (Heteroptera, Belostomatidae). *Comp. Biochem. Physiol.* 145A: 114–122.
- Sword, G.A. 2001. Tasty on the outside, but toxic in the middle: grasshopper regurgitation and host plant-mediated toxicity to a vertebrate predator. *Oecologia* 128: 416–421.
- Takegawa, H. and S. Takahashi. 1990. Allomonal secretions in six species of the genera *Periplaneta* and *Blatta* (Dictyoptera: Blattidae). *Jap. J. Environm. Entomol. Zool.* 2: 123–127.
- Teerling, C.R., D.R. Gillespie and J.H. Borden. 1993. Utilization of western flower thrips alarm pheromone as a prey-finding kairomone by predators. *Can. Entomol.* 125: 431–437.
- Terra, W.R. and A.G. de Bianchi. 1974. Chemical composition of the cocoon of the fly, *Rhychosciara americana*. *Insect Biochem.* 4: 173–183.
- Trigo, J.R. 2000. The chemistry of antipredator defense by secondary compounds in neotropical Lepidoptera: Facts, perspectives and caveats. *J. Braz. Chem. Soc.* 11: 551–561.
- Tringali, C. (ed.). 2012. *Bioactive Compounds from Natural Sources*. CRC Press, Boca Raton.
- Tschuch, G., P. Lindemann and G. Moritz. 2002a. Chemical defence in thrips. pp. 277–278. *In: R. Marullo and L. Mound (eds.). Thrips and Tospoviruses: Proceedings of the 7th International Symposium on Thysanoptera*. Calabria, Italy.
- Tschuch, G., Lindemann and G. Moritz. 2002b. Chemical defence in the thrips *Suocetathrips linguis* Mound and Marullo 1994 (Phlaeothripidae, Thysanoptera, Insecta). *Zoology* 105(Suppl. V): 99.
- Tschuch, G., G. Kießling, C. Engel, P. Lindemann and G. Moritz. 2004. Chemische Abwehr bei Thysanopteren, Mitteilungen der Deutschen Gesellschaft für Allgemeine und Angewandte Entomologie. 14: 183–186.
- Tschuch, G., P. Lindemann, A. Niesen, R. Csuk and G. Moritz. 2005. A novel long-chained acetate in the defensive secretion of thrips. *J. Chem. Ecol.* 31: 1555–1565.
- Tschuch, G., P. Lindemann and G. Moritz. 2008. An unexpected mixture of substances in the defensive secretions of the tubuliferan thrips, *Callococcithrips fuscipennis* (Moulton). *J. Chem. Ecol.* 34: 742–747.
- Turnbull, M.W. and N.J. Fashing. 2002. Efficacy of the ventral abdominal secretion of the cockroach *Eurycotis floridana* (Blattaria: Blattidae) as a defensive allomone. *J. Insect Behav.* 15: 369–384.

- Tyler, J., W. McKinnon, G.A. Lord and P.J. Hilton. 2008. A defensive steroidal pyrone in the glow-worm *Lampyrus noctiluca* L. (Coleoptera: Lampyridae). *Physiol. Entomol.* 33: 167–170.
- Unkiewicz-Winiarczyk, A. and K. Gromysz-Kalkowska. 2012. Ethological defence mechanisms in insects. III. Chemical defence. *Annales Universitatis Mariae Curie-Skłodowska Lublin—Polonia*, LXVII, 2, Sectio C: 63–74.
- Urbanek, A., R. Szadziewski, P. Stepnowski, J. Boros-Majewska, I. Gabriel, M. Dawgul, W. Kamysz, D. Sosnowska and M. Golebiowski. 2012. Composition and antimicrobial activity of fatty acids detected in the hygroscopic secretion collected from the secretory setae of larvae of the biting midge *Forcipomyia nigra* (Diptera: Ceratopogonidae). *J. Insect Physiol.* 58: 1265–1276.
- Vegliante, F. and I. Hasenfuss. 2012. Morphology and diversity of exocrine glands in lepidopteran larvae. *Annu. Rev. Entomol.* 57: 187–204.
- Vencl, F.V., N.E. Gómez, K. Ploß and W. Boland. 2009. The chlorophyll catabolite, pheophorbide a, confers predation resistance in a larval tortoise beetle shield defense. *J. Chem. Ecol.* 35: 281–288.
- Vilcinskas, A. 2011. *Insect Biotechnology*. Springer, Dordrecht.
- Vilcinskas, A. and J. Gross. 2005. Drugs from bugs: the use of insects as a valuable source of transgenes with potential in modern plant protection strategies. *J. Pest. Sci.* 78: 187–191.
- Viviani, V.R., J.W. Hastings and T. Wilson. 2002. Two bioluminescent diptera: the North American *Orfelia fultoni* and the Australian *Arachnocampa flava*. Similar niche, different bioluminescence systems. *Photochem. Photobiol.* 75: 22–27.
- Völkl, W., G. Hübner and K. Dettner. 1994. Interactions between *Alloxysta brevis* (Hymenoptera, Cynipoidea, Alloxystidae) and honeydew collecting ants: How an aphid hyperparasitoid overcomes ant aggression by chemical defense. *J. Chem. Ecol.* 20: 2901–2905.
- Vosseler, J. 1890. Die Stinkdrüsen der Forficuliden. *Arch. Mikroskop. Anatomie* 36: 565–578.
- Vršanský, P., D. Chorvát, I. Fritzsche, M. Hain and R. Ševčík. 2012. Light-mimicking cockroaches indicate tertiary origin of recent terrestrial luminescence. *Naturwissenschaften* 99: 739–749.
- Vuts, J., Z. Imrei, M.A. Birkett, J.A. Pickett, C.M. Woodcock and N. Tóth. 2014. Semiochemistry of the Scarabaeoidea. *J. Chem. Ecol.* 40: 190–210.
- Wagner, R., M. Aurich, E. Reder and H.J. Veith. 1990. Defensive secretion from larvae of *Apatania fimbriata* (Pictet) (Trichoptera: Limnephilidae). *Chemoecology* 1: 96–104.
- Wang, H. and T.B. Ng. 2002. Isolation of cicadin, a novel and potent antifungal peptide from dried juvenile cicadas. *Peptides* 23: 7–11.
- Weatherston, J. and J.E. Percy. 1978a. Venoms of Rhynchota (Hemiptera). pp. 489–509. *In: S. Bettini (ed.). Arthropod Venoms. Handbuch der Experimentellen Pharmakologie*, Vol. 48. Springer, Berlin.
- Weatherston, J. and J.E. Percy. 1978b. Venoms of Coleoptera. pp. 511–554. *In: S. Bettini (ed.). Arthropod Venoms. Handbuch der Experimentellen Pharmakologie*, Vol. 48. Springer, Berlin.
- Weatherston, I., J.A. MacDonald, D. Miller, G. Riere, J.E. Percy-Cunningham and M.H. Benn. 1986. Ultrastructure of exocrine prothoracic gland of *Datana ministra* (Druby) (Lepidoptera: Notodontidae) and the nature of its secretion. *J. Chem. Ecol.* 12: 2039–2050.
- Weidner, H. 1936. Beitrag zu einer Monographie der Raupen mit Gifthaaren. *Zeitschr. Angew. Entomol.* 23: 432–484.
- Weiss, M.R. 2006. Defecation behavior and ecology of insects. *Annu. Rev. Entomol.* 51: 635–661.
- Wheeler, C.H. and R.T. Cardé. 2013. Defensive allomones function as aggregation pheromones in diapausing ladybird beetles *Hippodamia convergens*. *J. Chem. Ecol.* 39: 723–732.

- Wheeler, J.W. and R.M. Duffield. 1988. Pheromones of Hymenoptera and Isoptera. pp. 59–206. *In*: E.D. Morgan and N. Bhushan Mandava (eds.). CRC Handbook of Natural Pesticides, Vol. IV, Pheromones, Part B. CRC Press, Boca Raton.
- Whitman, D.W. 1990. Grasshopper chemical communication. pp. 357–392. *In*: R.F. Chapman and A. Joern (eds.). The Biology of Grasshoppers. Wiley, New York.
- Whitman, D.W. 2008. Grasshopper sexual pheromone: a component of the defensive secretion in *Taeniopoda eques*. *Physiol. Entomol.* 7: 111–115.
- Whitman, D.W., M.S. Blum and D.W. Alsop. 1990. Allomones: chemicals for defense. pp. 288–351. *In*: D.L. Evans and J.O. Schmidt (eds.). Insect Defenses. State University of New York Press, Albany.
- Whitman, D.W., C.G. Jones and M.S. Blum. 1992. Defensive secretion production in lubber grasshoppers (Orthoptera: Romaleidae): Influence of age, sex, diet, and discharge frequency. *Ann. Entomol. Soc. Am.* 85: 96–102.
- Wiesner, J. and A. Vilcinskas. 2011. Therapeutic potential of antimicrobial peptides from insects. pp. 29–65. *In*: A. Vilcinskas (ed.). Insect Biotechnology. Springer, Dordrecht.
- Wigglesworth, V.B. 1974. The Principles of Insect Physiology. Chapman & Hall, London.
- Will, K.W., A.B. Attygalle and K. Herath. 2000. New defensive chemical data for ground beetles (Coleoptera: Carabidae): interpretations in a phylogenetic framework. *Biol. J. Linn. Soc.* 71: 459–481.
- Williams, B. 1986. Mandibular glands in the endoparasitic larva of *Uropsylla tasmanica* Rothschild (Siphonaptera: Pygiopsyllidae). *Int. J. Insect Morphol. Embryol.* 15: 263–268.
- Witz, B.W. 1990. Antipredator mechanisms in arthropods: A twenty year literature survey. *Flor. Entomol.* 73: 71–99.
- Wolf, S., H. Brettschneider and P.W. Bateman. 2006. The predator defence system of an African king cricket (Orthoptera: Anostostomatidae): does it help to stink? *Afr. Zool.* 41: 75–80.
- Wu, X., P.M. Flatt, H. Xu and T. Mahmud. 2009. Biosynthetic gene cluster of Cetoniacytone A, an unusual aminocyclitol from the endosymbiotic bacterium *Actinomyces* sp. Lu 9419. *Chem. Bio. Chem.* 10: 304–314.
- Wytenbach, R. and T. Eisner. 2001. Use of defensive glands during mating in a cockroach (*Diploptera punctata*). *Chemoecology* 11: 25–28.
- Yoshida, N., H. Sugama, S. Gotoh, K. Matsuda, K. Nishimura and K. Komai. 1999. Detection of ALMB-toxin in the larval body of *Myrmeleon bore* by anti-N-terminus peptide antibodies. *Biosci. Biotechnol. Biochem.* 63: 232–234.
- Yoshida, N., K. Oeda, E. Watanabe, T. Mikami, Y. Fukita, K. Nishimura, K. Komai and K. Matsuda. 2001. Chaperonin turned insect toxin. *Nature* 411: 44.
- Yu, X.-P., J.-L. Zhu, X.-P. Yao, S.-C. He, H.-N. Huang, W.-L. Chen, Y.-H. Hu and D.-B. Li. 2005. Identification of *anrF* gene, a homology of *admM* of andrimid biosynthetic gene cluster related to the antagonistic activity of *Enterobacter cloacae* B8. *World J. Gastroenterol.* 11: 6152–6158.
- Zhang, Q.H., K.R. Chauhan, E.F. Erbe, A.R. Vellore and J.R. Aldrich. 2004. Semiochemistry of the goldeneye lacewing *Chrysopa oculata*: Attraction of males to a male-produced pheromone. *J. Chem. Ecol.* 30: 1849–1870.
- Zhao, X., Q. Meng, L. Yu and M. Li. 2009. Composition and bioactivity of secretion from *Stauronematus compressicornis* (Fabricius). *For. Stud. China* 11: 122–126.
- Zhu, J., R.C. Unelius, K.-C. Park, S.A. Ochieng, J.J. Obrycki and T.C. Baker. 2000. Identification of (Z)-4-tridecene from defensive secretion of green lacewing *Chrysoperla carnea*. *J. Chem. Ecol.* 26: 2421–2434.
- Zimmer, M.M., J. Frank, J.H. Barker and H. Becker. 2006. Effect of extracts from the Chinese and European mole cricket on wound epithelialization and neovascularization: *in vivo* studies in the hairless mouse ear wound model. *Wound Repair Regeneration* 14: 142–151.
- Zwick, P. 1980. Plecoptera, Steinfliegen. *Handbuch der Zoologie, II. Bd. 2. Hälfte, 2. Teil, 7. Part. de Gruyter, Berlin.*